Department of Chemical Engineering

Studies on the Pre-Treatment of Palm Oil Mill Effluent

Florence Wong Pin Sing

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Declaration

"To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made. This thesis contains no material which has been accepted for the award of any other degree or diploma in any university".

Signature Date

_____ _____

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ABSTRACT

The feasibility of using hydrochloric acid (HCl), heat, dilution and magnetic stirring for the pre-treatment of palm oil mill Effluent (POME) before the primary anaerobic treatment was investigated in this study. The theoretical background of oily water emulsion which is the characteristic of POME was reviewed. A range of experiments was performed on samples made up of different combinations of the three major components of POME namely, palm oil, solid from decanter and water. The results suggest that the development of a pre-treatment system to remove the 0.5- 1.2% residue oil and 3-4% solid matter from the fresh POME is feasible thus it could improve the efficiency of further downstream POME treatment.

Experiments were conducted to examine the rate of oil flotation from the mixtures of different ratios of palm oil and water treated with different concentrations of HCl, and temperatures and magnetic stirring. Similarly, a series of experiments were performed to determine the rate of solid settlement from palm oil-solid mixture, solid-water mixture and palm oil-solid-water mixture of different ratios treated with different concentrations of HCl and different temperatures. The data obtained from the experiments were used to determine the optimum dosage of HCl used and the temperature required for best oil recovery and solid settlement.

From the kinetic studies, the models of the kinetic rate of palm oil flotation and solid settlement were derived. A macro kinetic modeling was adapted to the oil flotation while a power model was used for solid settling. The results showed that treatment with 0.5% HCl was sufficient to increase the rate of oil flotation significantly in Palm oil-water mixture. However, the effect was dependent on the oil-water ratio. An increase in temperature gave higher rate of oil flotation but not as great as that of HCl treatment. Dilution was found to be the two other factors that affected the rate of flotation. The solid settling rates in all tested samples were not significantly affected when they were treated with HCl. The rate of solid settlement was found to be temperature dependent. The optimum temperature for the rate of solid

sedimentation was found to be in the region of 80^0C. Similar positive effect was also observed for a more diluted sample of Solid-Palm oil-Water mixture.

Nomenclature

POME	Palm Oil Mill Effluent
BLD	Bintulu Lumber Development Sdn Bhd
HCl	Hydrochloric Acid
DLVO	Derjaguin, Landau, Verwey and Overbeek
HRT	Hydraulic Retention Times
VOC	volatile organic compounds
R_f	Rate of oil flotation, (*g/ml/min*)
C_o	Oil concentration inside the oil-water emulsion, (*g/mL*)
n	Kinetic order
k	Constant
V_i, V_e, V_o	Volumes of total oil, oil-water emulsion, and oil layer respectively, (*mL*)
ρ_o	Oil density, (g/cm^3)
t	Time, (*min*)
dV/dt	Rate of change of volume
V_s	Solid settling velocity, (*cm/min*)
A_c	Area, (cm^2)
BOD	Biological oxygen demand
COD	Chemical oxygen demand
VFA	Volatile fatty acids

HAP	Hydrolysis and acidogenesis process
HRT	Hydraulic retention time
G	Free energy
H	Distance between particles
A	Surface area of the particles
g	acceleration of gravity
ρ_f	density of the fluid
η	dynamic viscosity of the fluid
r	radius of the particles
β	volume fraction of solid

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Chapter 1

Introduction

1.1 Background

Oil palm, (Eleasis guineensis jacq) is Malaysia's golden crop and has become one of the key income revenues for the country in the recent decades. As shown in Figure 1.1, Malaysian palm oil industry is expanding rapidly over the years. The total exports of oil palm products, consisting of palm oil, palm kernel oil, palm kernel cake, oleo-chemicals, biodiesel and finished products in year 2.10 amounted to 23.06 million tonnes and generated 59.77 billion ringgit in total export earnings (MPOB: Over-view of Malaysian Oil Palm Industry 2010). This industry is providing large employment opportunities not only for Malaysians, but also people from neighboring countries, especially Indonesia.

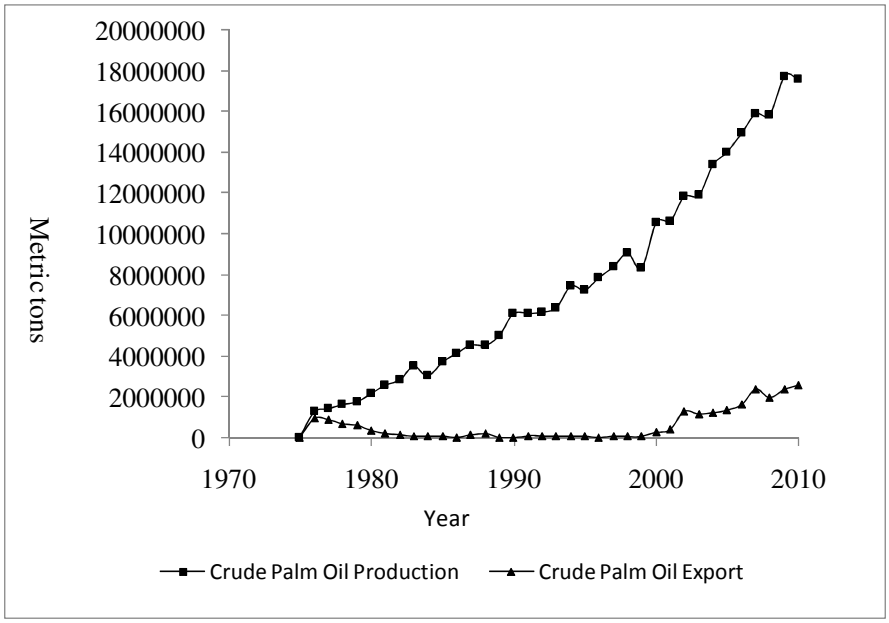


Figure 1.1: Palm Oil Production and Exports for Malaysia, 1975-2008 (Department of Statistics, Malaysia: 1975-1989, MPOB: 1990-2008)

The ratio of world palm oil production as compared to other oil and fats has increased from 23% in year 2004 to 24% in year 2006 as shown in Table 1.1 and the world consumption of Palm and palm kernel oil as shown in Figure 1.2 is growing faster in comparison to other oils and fats too.

While Malaysia enjoys the economic benefit from the vast production of palm oil, the impact of the production of a huge volume of waste products has also become a worrying consequent. The process flow chart in Figure 1.3 shows the sources of the major waste products from the extraction process of palm oil.

Table1.1 World Production of 17 Oils and Fats: 1999-2008 ('000 Tonnes)

Oils/Fats	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**
Palm Oil	20,625	21,867	23,984	25,409	28,259	30,987	33,846	37,142	38,674	43,118
Palm Kernel Oil	2,559	2,698	2,947	3,044	3,347	3,581	3,976	4,344	4,496	4,989
Soya bean Oil	24,794	25,563	27,828	29,850	31,241	30,729	33,612	35,278	37,354	37,164
Cottonseed Oil	3,893	3,850	4,052	4,221	3,987	4,367	4,978	4,903	5,043	5,029
Groundnut Oil	4,697	4,539	5,141	5,178	4,508	4,706	4,506	4,382	4,194	4,445
Sunflower Oil	9,308	9,745	8,200	7,610	8,917	9,423	9,785	11,191	10,843	10,687
Rapeseed Oil	13,247	14,502	13,730	13,343	12,698	15,088	16,294	18,510	18,746	19,847
Corn Oil	1,935	1,966	1,962	2,016	2,017	2,025	2,133	2,264	2,319	2,408
Coconut Oil	2,399	3,261	3,499	3,098	3,270	3,040	3,237	3,083	3,114	3,130
Olive Oil	2,475	2,540	2,761	2,773	2,904	3,110	2,965	2,798	3,020	3,081
Castor Oil	435	497	515	438	425	500	540	535	524	603
Sesame Oil	686	705	747	807	810	831	868	860	831	803
Linseed Oil	734	705	648	581	594	635	626	695	693	643
Total Vegetable Oils	**87,787**	**92,438**	**96,014**	**98,368**	**102,977**	**109,022**	**117,366**	**125,985**	**129,851**	**135,947**
Butter	5,885	5,967	6,010	6,331	6,394	6,476	6,666	6,730	6,918	7,123
Tallow	8,171	8,202	7,693	8,062	8,018	8,230	8,386	8,548	8,538	8,585
Fish Oil	1,413	1,411	1,131	946	1,005	1,129	988	1,001	1,057	1,076
Lard	6,619	6,739	6,780	7,016	7,228	7,367	7,577	7,855	7,632	7,740
Total Animal Oils/Fats	**22,088**	**22,319**	**21,614**	**22,355**	**22,645**	**23,202**	**23,617**	**24,134**	**24,145**	**24,524**
GRAND TOTAL	**109,875**	**114,757**	**117,628**	**120,723**	**125,622**	**132,224**	**140,983**	**150,119**	**153,996**	**160,471**

Source: Oil World Annual (1999 - 2008) & Oil World Weekly (2008) MPOB - For data on Malaysian palm oil and palm kernel oil.

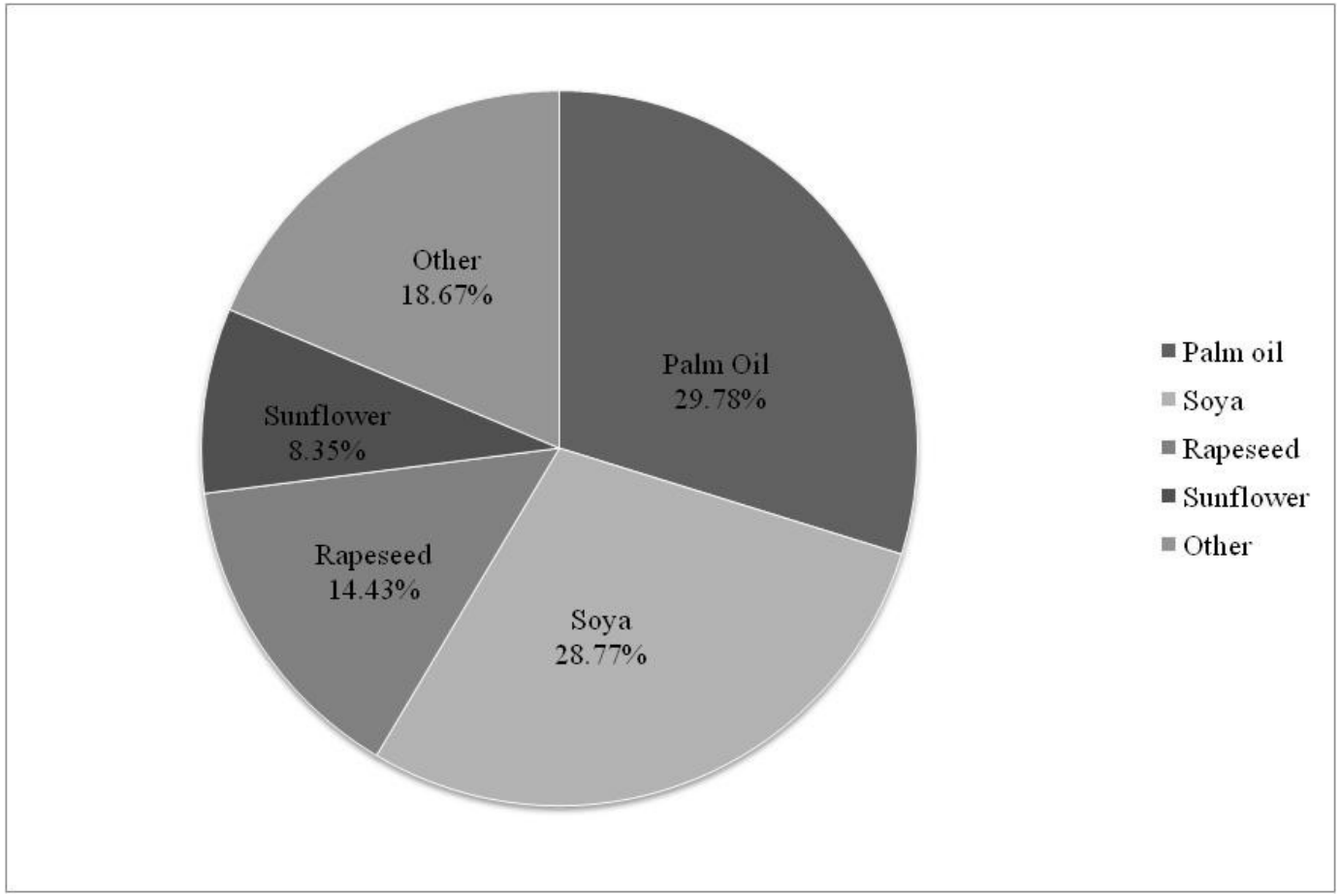


Figure1.2: Share of the Vegetable Oil Market 2007/2008: The growing popularity of palm oil as edible Oil. Source: MPOB and Oil World.

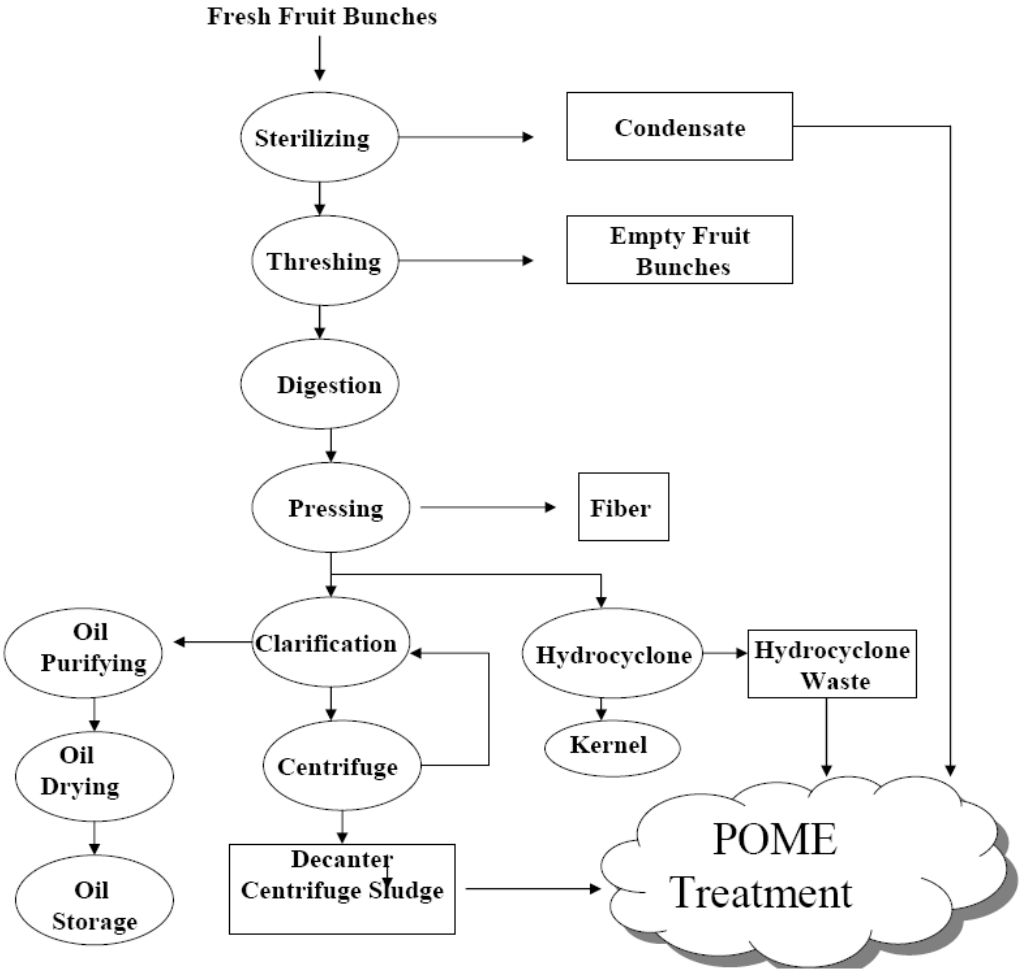


Figure1.3: Palm Oil Process Flow chart (Lam and Lee, 2011)

As described in figure 1.3, POME is made up of sterilizer condensate (10% to FFB), hydrocyclone wastewater (2% to FFB) and the liquid sludge from the decanter (35% to FFB) during the extraction process of palm oil from the fresh oil palm fruit bunches.

This research aims at the investigation on the treatment of POME formed mainly from the liquid sludge of the decanter combined with some sterilizer condensate and hydro-cyclone water. With the high Biochemical oxygen demand of POME, this water pollutant is hazardous besides its non-toxic characteristics. In Malaysia, the Department of Environment enforces the regulation for the discharge of effluent from the crude palm oil industry under the Environmental Quality (Prescribed Premises) (Crude Palm Oil) Order and Regulations 1977 (Thani, Ibrahim, and Sulaiman 1999). Section 25 (1) of this Act states clearly the requirement of any Palm Oil Mill owner to apply for a licence to emit, discharge, or deposit any wastes into any inland waters in contravention of the acceptable conditions specified under section 21 and a licence to discharge wastes into Malaysian waters under section 29 (1).

While Biological pond treatment processes are widely applied to treat POME, their applications however, have some limitations such as:

1. Long hydraulic retention time (HRT) that holds up large volume of water from the environment. (Wong and Wong 2002).
2. Inability in responding to great fluctuations in feeding rate due to high and low crop seasons. (Wong and Wong 2002).
3. Rainfall patterns that affect the operations of the ponds and silting that reduces the HRT of the ponds and hence their performance (Wong and Wong 2002).

As a result, proper maintenance, close monitoring, skilled personnel and commitment from management are required. Thus, a more efficient treatment system is highly desirable in all palm oil mills in order to control the discharge of effluents to any bodies of water. Literature review showed that a wide range of research have been presented in an attempt to achieve this. Membrane filtration is one of them. Other methods such as dissolved air flotation, evaporation technology had also been studied. However, each of them has its own shortcomings in different aspects besides its technical advantages. Many of them can only be applied for the secondary treatment after the anaerobic treatment which does not help much in improving the overall efficiency. Therefore, most of the palm oil mills in Malaysia are still not ready to abandon the pond system for

a totally new system. In an attempt to help improving the above situation, this study aims at investigating the characteristics and behavior of the different components of POME under different designed treatment conditions. The knowledge obtained can be used to evaluate the feasibility of a physical-chemical pre-treatment process for raw POME from the palm oil mill before it is passed into the anaerobic treatment system.

1.2 Aims and Objectives of this thesis

The aim of the research study is to develop an effective physical-chemical method for the pre-treatment of POME.

The objectives of the work are as follows:-

1. To evaluate the feasibility of treating POME at a laboratory scale with HCl at elevated temperature to enhance oil recovery and solid settlement.
2. To determine the dosage of HCl used and temperature required for optimal oil recovery and solid settlement.
3. To examine the electromagnetic field on the effect of separation of oil and solid particles in the POME mixture.
4. To establish a kinetic model for rate of oil flotation and solid settlement for the POME mixture.

1.3 Scope of Study

The scope of research will cover three areas of investigation. The first area of study will focus on the effect of temperature and varying HCL concentrations on enhancing the flotation rate of the specified POME mixtures. The second area of study will involve experimental work to determine the effect of temperature and varying HCL concentrations on enhancing the settlement rate of the solid particles in the specified POME mixtures. In association with the above experimental studies, the third area of work will be performed to develop the kinetic models for the rate of floatation and sedimentation of solid particles in the POME mixture.

1.4 Thesis Overview

Chapter 1 includes an introduction to the background of oil palm industry in Malaysia and the aim and the objectives of this thesis, the scope of study and the thesis overview. In Chapter 2 a background on the existing POME treatment systems in Malaysia is reviewed. A framework of the proposed POME treatment system is included and past studies by other researchers on the separation of oil and solids from POME are discussed. The emulsion characteristics of general oily wastewater and POME are also presented. For Chapter 3, the research methodology and the results obtained for the effect of HCl, heat and magnetic stirring treatments on the oil flotation rate for crude palm oil-water mixture and refined palm oil-water mixture are described. The modeling of the oil flotation rate from the experimental results obtained is presented in this chapter. In Chapter 4, the results obtained for the effect of HCl and heat treatments on the solid settling rate for solid-crude palm oil mixture are discussed. The modeling of the solid settling rate from the experimental results obtained is presented. Similarly, data analysis is carried out on the results obtained for the effect of HCl and heat treatments on the solid settling rate for the decanter solid-water mixture and solid-palm oil-water (Clarifier sludge-water) mixture in Chapter 5. The modeling of the solid settling rate from the experimental results obtained will be presented in this chapter. The last chapter presents the conclusions and outlines summary of the studies, and a proposal of a pre-Treatment Scheme for POME

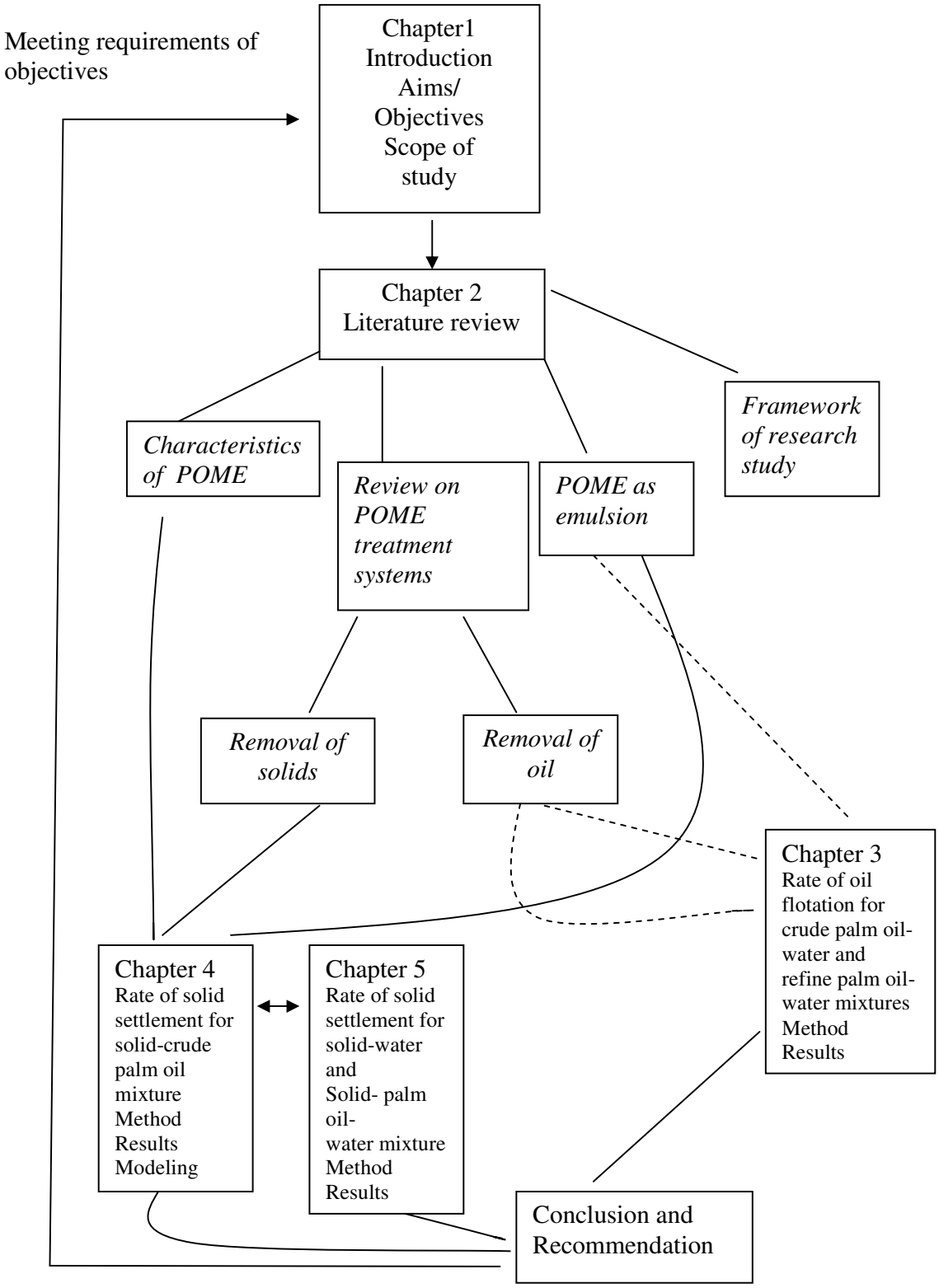


Figure 1.4: Flow chart of Thesis Over-view.

Chapter 2

Literature Review

2.1 Characteristics of POME

Figure 1.3 shows that POME is one of the major wastes of a palm oil processing mill formed mainly from the liquid sludge of the decanter and with some sterilizer condensate and hydro-cyclone water. With approximately 1.9 metric ton of POME generated from every metric ton of palm oil produced (BLD 2006), the amount of POME generated from the production of 20 million metric tons in year 2006 would be 38 million metric tons. Fresh POME is usually thick brownish slurry of temperature around 80 to 90^{o}C, and with a pH value of 3.8 to 4.5. It contains a very high concentration of organic matter (COD = 40, 000 to 50, 000 mg/L, BOD = 20, 000 to 30, 000 mg/L). The effluent is non-toxic as no chemical is added in the oil extraction process (Zinatizadeh et.al 2005). It is formed by pumping and flushing of oil, water and solid mixture into tanks mechanically. It is a liquid waste consisting of 93-95% of water, 5-7% of non-oily solid matter and 0.9-1.5% oil. These oil droplets in POME are solvent extractable. The extract of the oil droplets consists of 84% neutral lipids and 16 wt% of complete lipids (6 wt% glycolipids and 10 wt% phospholipids). The neutral lipids consist of 74.7% triglycerides. 8% diglycerides, 0.5% monoglycerides and 0.8% free fatty acids (Chow and Ho 2002). The solids are made up of rod like particles of colloidal dimensions, plant cell debris and ruptured cell wall, crystal like particles, and light polarized fiber and sand (Ho and Tan 1983). The characteristics of POME are usually presented by the parameters listed in Table 2.1.

Table 2.1 Characteristics of POME and its respective standard discharge limit (Ahmad et al. 2003)

Parameter	Concentration, mg/L	Standard Limit, mg/L
Temperature (^{0}C)	75-90	-
pH	4.7	5-9
Oil and grease	4,000	50
BOD	25,000	100
COD	50,000	-
Total Solids	40,500	-
Suspended Solids	18,000	400
Total Nitrogen	750	150

2.2 Review on POME Treatment

2.2.1 The Current Process

Figure 2.1 shows a schematic diagram of the general POME treatment system used by 85% of palm oil mills in Malaysia (Ang and Leong 1984). Liquid waste coming from the sterilizer, decanter and hydrocyclone of a palm oil mill is collected at the sludge pit to form the general waste called POME. The discharge of POME from sludge pit to the de-oiling pond is regulated such that it allows the POME to stay in the de-oiling pond for 30 days. The free oil separated from POME in the de-oiling pond is usually skimmed off and sold as sludge oil. The de-oiling process can be done in a pond or by dissolved air flotation or by flocculation process.

The following step is the anaerobic treatment process. The retention time for POME in the anaerobic pond usually lasts for 70 days. Here, the methanogenesis and acidification processes by the anaerobic bacteria takes place to break down the organic matter and

methane gas, Hydrogen sulfite and carbon dioxide will be released to the air. Some degraded oil may float to the top of the waste water after being separated from the degraded organic matter and some solid will settle to the bottom. The usual practice of anaerobic pond system is replaced by anaerobic digestion tanks by some millers in Malaysia. The facultative pond is a transition station for anaerobic and aerobic treatment of POME. Aerobic ponds are placed where the aerobic bacteria further breaks down the remaining organic matter to allow more settling of solid and result in clearer water. Aerators are usually installed to facilitate the aeration process. Continuous or batch aeration tanks are used in place of aeration ponds by some millers nowadays. Polishing systems installed with filters and aerators are often used nowadays for further reduction of suspended solids and Biochemical Oxygen Demand (BOD) in the treated POME before discharging it into the water course. As a whole, the existing process of POME treatment takes about 120-200 days to obtain the water that meets the requirements of the Department of Environment in Malaysia (Wong 2002).

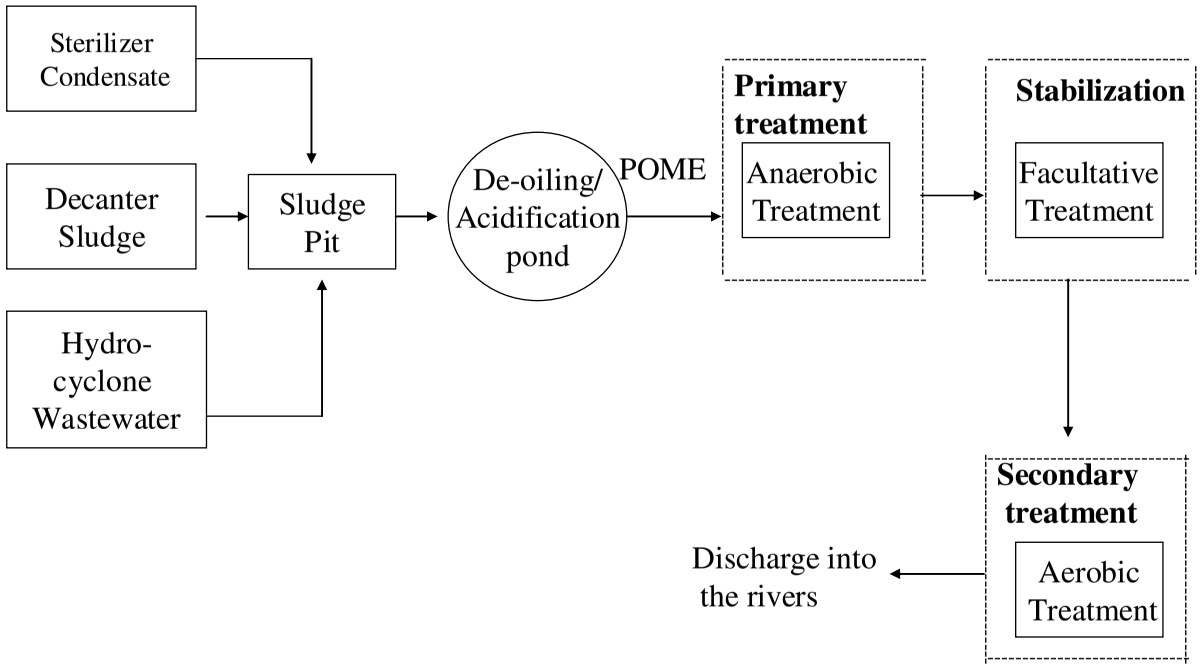


Figure 2.1 a Flow Chart of the General POME Treatment System

2.2.2 Removal of Solids

With the understanding of the existing POME treatment as described in Section 2.2.1, it is very clear that improvement needs to be done to shorten the treatment time, to reduce the green house gas (methane, hydrogen sulfite and carbon dioxide) emission to the air and to ensure a faster release of useable water into the environment. From literature review, many researchers appear to have similar view about the importance of an efficient solid and oil removal method to enhance a more efficient POME treatment. A few of those developed methods are discussed here to help our investigation in this study. The following are examples of Solid Removal Systems:

Electroflotation

Solid removal from POME using **Electro-flotation by Lead Dioxide-coated titanium Anode** proves to have a fairly high rate of removal of 86% of suspended solids and a reduction of half of the dissolved substances under prolonged electrolysis, (Ho and Chan 1986). However, this method has to operate at pH 10 and for 20 hours at laboratory scale. Therefore, lime has to be used to adjust an average POME PH of 4.5 to 10. The amount of lime used was not reported in this study.

The study concentrates on the removal of solid. The COD and the suspended solids content of the electrolyzed dispersion were still too high for direct discharge into waterways. The method could be made part of a pre-treatment system as described in Figure 2.2 whereby the resulting electrolyzed dispersion would be amenable to secondary treatment such as mechanical aeration to bring it to within the permitted level of effluent standards. The economic operational feasibility at industrial scale of this method has not been fully investigated. . No palm oil mill in Malaysia is known of adopting this treatment method.

Membrane treatment

Membrane treatment is another method that has been studied at pilot scale for POME treatment. This system operates in conjunction with an anaerobic reactor can produce clear effluent water even for reusing at boilers and the mills. However, it will only work well if the raw POME has been pre-treated either chemically or anaerobically. If the

membrane filters the feed water pre-treated by efficient chemical flocculation and activated carbon, it produces clear and odorless water discharge. If it filters feed from anaerobic reactor, it helps to retain sufficient quantity of active biomass in the anaerobic reactor to cope with erratic incoming loading rate. The problems encountered by membrane system are fouling of the membrane even within 10 to 40 minutes of use. Increased cross-flow velocity will reduce the percentage of rejection and thorough cleaning is required for reuse of the membrane (Fakhru'l-Razi and Noor 1999).

Evaporation Technology

Evaporation technology is a treatment system that utilizes steam heat to evaporate the water in POME to produce dry solid for land application in the oil palm estate and water distillate for recycle. It was found that with 3-4% total solids in POME feed, about 85% of the water in the POME can be recovered as distillate. There is no recovery of oil by this method and the energy requirement is a major constrain in this process. It was found that one kg of steam is required to evaporate one kg of water content in POME *(*Ma 2000*)*.

Dissolved Air Flotation

This method uses pumps to feed the raw POME pre-treated with chemical flocculants into a vessel under high pressure and injects air into the incoming recycled water. The dissolved air bubbles will help carry the solid POME sludge to the top of the tank and be scraped to a trough from where it would be removed from the Dissolved Air flotation unit. Clarified effluent will overflow into a holding tank where a portion of it will be recycled into the pressure tank while the excess is discharged. The results from the study suggested that it was technically feasible to use Dissolved Air Flotation for liquid-solid separation in POME treatment. A total suspended solid and BOD removal of more than 90% and 80% respectively can be achieved. To achieve this, however, requires a very high operating cost because very high pressure and long hydraulic retention time (HRT) in the pressure vessel is required, if the recycled water instead of portable water is used to carry dissolved air into the flotation chamber. It is not a sustainable approach to use portable water in such an operation. Another constrain of this method is that it

performs well at a much lower surface loading rates as compared to the typical effluent flow rates typical of palm oil mills. Very large facilities will be required if Dissolved Air Flotation is used to treat effluent of such high surface loading rates. Also, if this treatment method is used to treat POME, post- dissolved air flotation treatment would be required before the effluent can be discharged into the river course. This means the effluent would have to go through the whole cycle of anaerobic and aerobic treatment again. This suggests that the Dissolved Air Flotation method may be of limited use in POME treatment (Ng, Goh and Tay 1988).

The treatment systems as described above showed treatment on solid removal in either primary or secondary treatment stage. Figure 2.2 and 2.3 however show the location of solid and oil removal process to be done among the different stages of POME treatment process in this research in order to speed up the overall treatment process. The Pre-treatment by removal of solid and oil is to be located at the de-oiling stage shown in Figure 2.1

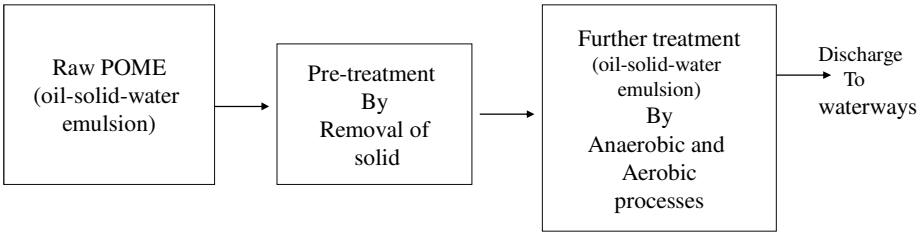


Figure 2.2 Flow-charts for Pre-treatment by removal of solid process.

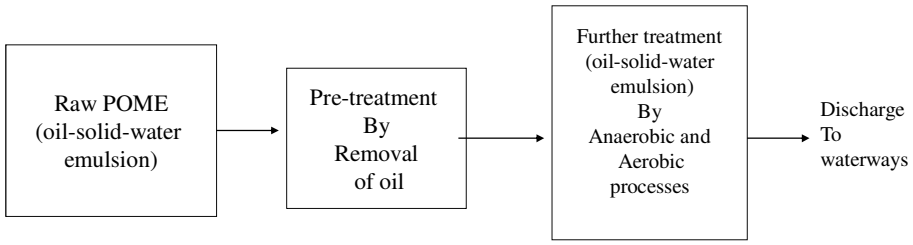


Figure 2.3 Flow-chart for Pre-treatment by removal of oil

2.2.3 Removal of Oil

The removal of oil in the pre-treatment of POME is very important because besides the high content of organic matter (BOD: 25,000mg/L) that cause the slow degradation rate of POME, the high content of oil and grease (4,000mg/L) is also a cause that slows down or inhibit the microbial degradation process of the organic matter (Hanaki, Matsuo, and Nagase 1981), if POME is sent directly for the anaerobic treatment in its raw state. The emulsified and dissolved vegetable oils (glycerol triesters) will hydrolyze to long chain fatty acids and glycerol under anaerobic conditions. While slowly degradable under anaerobic conditions, the long chain fatty acids may also inhibit anaerobic microbial activities. There were researchers who had similar insights for improving the efficiency of POME treatment and had done studies on applying different methods to remove oil and grease from POME before discharging for further treatment. Some of them are described below. Figure 2.3 shows the location of oil removal process

to be done among the different stages of POME treatment process in order to speed up the overall treatment process. Some reports on oil removal methods are discussed below.

Solvent extraction

A study is done to compare a few different solvents on their efficiency on extraction of oil using soxhlet extraction method. This method proved to be one of the effective methods in reducing the content of oil and grease in palm oil mill effluent. The results in the research done by (Ahmad et. al 2003) showed that n-hexane is the best organic solvent to extract the oil and grease content from POME followed by benzene, petroleum benzene, petroleum ether, pentane and n-heptane. By using n-hexane as the solvent, it is estimated that about 0.54 grams of oil and grease per liter of POME can be extracted with optimum conditions applied. The optimum solvent to POME ratio is 6:19, optimum mixing speed is 200rpm, optimum mixing time is 20 minutes and optimum pH is 9. This shows that large amount solvent is needed to recover a very small amount of oil. Chemicals are also required to adjust the PH from about 4.5 to 9. Besides, organic solvent is flammable and easily evaporates. N-hexane is inedible, so oil extracted cannot be consumed. Therefore, this might not be a practical method for removing oil and grease during the pre-treatment of POME

Chitosan adsorbent

The comparative study on the residual oil and suspended solid removal using natural adsorbents chitosan, bentonite and activated carbon showed that Chitosan gives the best performance among the three in terms of dosages used and the amount of oil and suspended solid removal (Ahmad et. al, 2005). Chitosan has amine functional groups, which attracts anionic ions; therefore it could easily bind and bridge into flocs. The overall charge of chitosan is positive; whereas residue oil is negative, therefore, attractions between the charges enhance the agglomeration process. This mechanism is called charge neutralization and was studied by Jill et al. (1999). Hence, chitosan not only acts as an adsorbent but at the same time as a coagulant to agglomerate the residual oil. However, this method has only been done on lab scale. Its performance at pilot and commercial scale is yet to be demonstrated (Ahmad et. al, 2005).

Rubber powder absorption

Another study on oil and grease removal is by adsorption of residue oil from palm oil mill effluent using rubber powder. 30mg/dm^{-3} of rubber powder is required to reduce 80% of residue oil in POME with a mixing rate of 150rpm and a mixing time of 3 hr and pH 7. Again, chemical is required to adjust the PH from 4.5 to 7 and further studies are required to investigate on the possible recycling of the rubber powder which can become another waste product. (Ahmad et al. 2005).

2.3 POME as Emulsion

2.3.1 Formation of POME Emulsion

The formation of POME emulsion, consisting of oil-solid-water phase mixture has been implicated during the pre-treatment process of crude POME (Kemmer 1988). The existence of this oily wastewater emulsion could pose a real challenge for effective removal or separation of oil from the fine solid particles or water. Generally, emulsion is a heterogeneous system that consists of at least one immiscible liquid intimately dispersed in another liquid in the form of droplets. It is formed by oil mixing with water due to shear that can result from the oily wastewater traveling through a pump and splashing into a tank and anything that will break up and disperse larger oil droplets into oil droplets with size ranging from 20-150 micron in diameter (Alther 2001). The POME emulsion was believed to be formed by mechanical pumping and flushing through different processing machineries, pipes and tanks during crude palm oil extraction process. The typical liquid waste consists of 93-95% of water, 5-7% of non-oily solid matter and 0.9-1.5% oil. The pumping and flushing process breaks oil into minute droplets and generates negative charges on the surface of the droplets. This causes the oil droplets to repel one another and disperse them into the continuous water phase to form the emulsion. The POME emulsion is thought to be stabilized by the negative charges on the surface of the oil droplets and fine solid particles present as illustrated in Figure 2.4 (Kemmer 1988). In chemical emulsions, usually a surfactant, detergent or soap is present as an emulsifier. Surfactants consisting of a hydrophilic/oleo-phobic end

and a hydrophobic/oleophilic end could act as a coupling agent between the oil/water phases.

Studies by Chow and Ho (2002) demonstrated that the oil droplets in POME were solvent extractable and the surface active compounds like phospholipids and glycolipids that have been shown to be present could itself stabilize the dispersion of oil droplets in the continuous water phase. The oil is believed to be mostly trapped in the suspended solids and inseparable mechanically. The suspended solid particles that constitute the rod like particles of colloidal dimensions are derived from plant cell debris and ruptured cell wall, and this crystal like particles, and light polarized fiber and sand were suggested to function as coating layer of finely divided solids around the oil droplets (Ho and Tan 1983). These particles may also function as bio-surfactant (stabilizing agent) because of the presence of cellulose and phospholipids, and thickener (that increases viscosity of water) such as the gum from the plant cells.

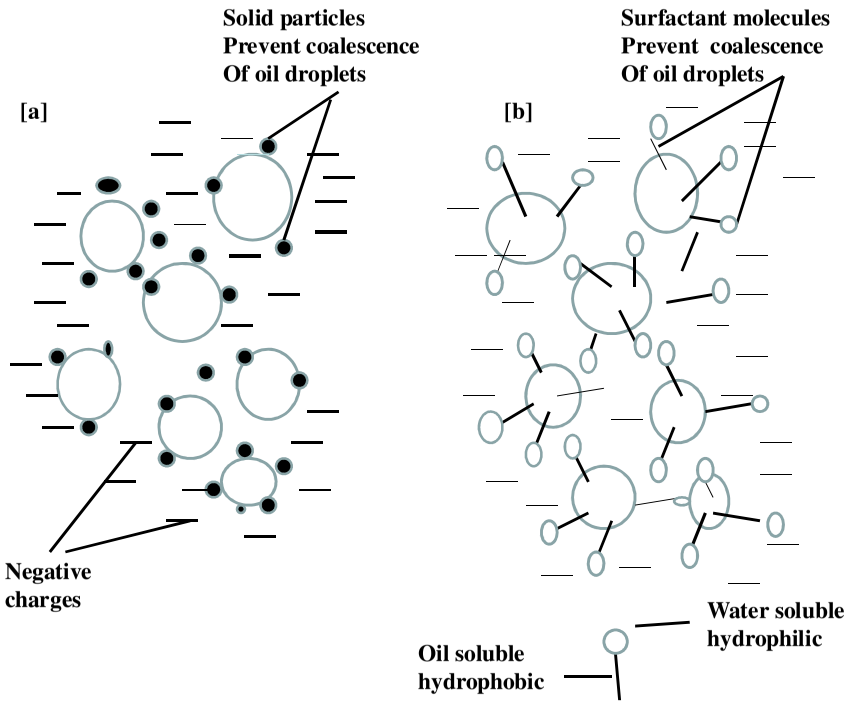


Figure 2.4a: Oil-water emulsion stabilized by negative charges and fine solids

Figure 2.4b: Oil-water emulsion stabilized by surfactants (Kemmer 1988)

2.3.2 Stability of emulsions

It is important to understand the energetic and the factors that contribute to the stability of emulsions because they will have implications on the effective methods used for the pre-treatment of POME. A stable emulsion is one where small droplets of oil are dispersed within the water and are prevented from coalescing. Coalescing and settling of the dispersed oil droplets and solid particles respectively would occur very slowly or not at all. As described in (Kemmer 1988), mechanically generated repulsive electrical charges, presence of surfactants and emulsifiers and finely divided solids are the most common agents that enhance the stability of an emulsion. The stability caused by the repulsive electrical charges can be explained by Derjaguin, Landau, Verwey and Overbeek (DLVO) theory which stated that the dispersed particles are subject to two independent forces: the van der Waals force of attraction and the electrostatic force of repulsion arising from the presence of electrical double-layers at the particle surfaces.

The net interaction between the particles is obtained by summing these two terms. If the repulsion potential exceeds the attraction potential, an energy barrier opposing collision occurs. If the magnitude of this energy barrier exceeds the kinetic energy of the particles, the suspension is stable. The van der Waals negative potential becomes significant only when the distance between the particles is quite small. The free energy involved in the process can be expressed in the following equation:

$$\Delta G = \Delta H^{'} = 2\sigma^{o} A \qquad (2.1)$$

Where G = Free energy

H = Distance between particles

A = Surface area of the particles

σ^0 = Surface or interfacial tension (Everett, 1988).

The role of the emulsion stabilizing factors such as surfactants, finely divided solids and others as mentioned above will be described in the following sections in order to give insights to the objectives of this research study in treating POME as it is designed.

The role of surfactants

In an oil-water emulsion, stabilizing effect of surfactants and emulsifiers is the result of the lowering of interfacial tension caused by an increase in the interfacial area after the breaking and dispersion of oil droplets into the water phase. The interfacial area is lower if the two phases stay separate. Energy is involved in keeping the oil droplets to stay at a distance from one another and it is not natural to maintain a high interfacial area than its normal state. The energy involved is measured as interfacial tension (Walstra 1993). To maintain the emulsion, this interfacial tension has to be lowered and the surfactants and emulsifiers of various types (ionic, anionic and non-ionic) are able to do this. Srivastava (1961) reported **t**he permanence of an emulsion is determined by the nature of the surfactant or emulsifier film, but its other physical characteristics and adsorption of the ions on the film resulting in electrical forces at the interface are the criteria which seem to have a direct bearing on emulsion stability. The surface active compounds like phospholipids and glycolipids present in POME are believed to act as emulsifiers and contribute to its emulsion stability.

1. **Phospholipids and proteins**

The surface active compounds like phospholipids and glycolipids present in POME might act as emulsifiers in stabilizing the emulsion. Besides, the proteins from the cell debris present in POME may contain surface active ingredients that can stabilize the emulsion state. Proteins containing surface active ingredients have been utilized as emulsifiers in food products for many years (Dickinson and McClements 1995; Thanasukarn, Pongsawatmanit and McClements 2004). However, protein-stabilized emulsions are highly sensitive to environmental stresses such as pH, ionic strength and temperature (Das and Kinsella 1989; McClements 2004). The sensitivity of protein stabilized emulsion could be attributed to the neutralization of charges present in the proteins due to pH changes (McClements 1999). Others attributed the destabilising of emulsion to the interactions between proteins and phospholipids that lead to changes in surface activity, modifications on protein structure and net charge (Van Nieuwenhuyzen and Szuhaj 1998).

2. Finely divided solids

Besides proteins and phospholipids, many reports have documented the involvement of the finely divided solid particles in stabilizing the oil-water emulsion (Hunter et al 2008; Rousseau 1999; Velev and Lenhoff 2000). The silica powder, various clays, basic salts and plant cell fragments are among some of these fine particles. They are very small size, as compared to the size of the dispersed oil droplet and they act by forming a coating layer around the dispersed oil droplets (Kemmer 1988; Tan, Gee and Stevens 2003). This coating layer will work as a barrier for the oil droplets to come near to each other and coalesce as illustrated in Fig 2.4. This prevents the separation of oil and water from the emulsion and thus stabilizes it. Levine (1988) and Iler (1979) had reported in greater details on the stabilization mechanisms of such coating layer of finely divided solids. Yan (1996) explained the stabilizing effect of finely divided solids in terms of contact angle of the solid particles at the oil-water interface. A contact angle of 90^{o} was found to result in a most stable emulsion.

Other factors

The natural occurring electrostatic effects present between oil droplets and water is another contribution to the stability of emulsions. The surface potential of oil droplets in water was measured in the absence of any surfactants and it was found that the interface between pure oil and water phases bears a considerable negative surface potential of -60 mV (Carruthers 1938). The negative surface potential has been attributed to the adsorption of hydroxyl ions from the water to the water-oil interface (Dickson 1941; Marinova et.al. 1996; Taylor and Wood 1957). It is interesting to note the charge of the air-water interface can be considerable and sometimes, high enough to stabilize free aqueous films without any surfactant (Bergeron 1996; Exerowa and Zacharieva 1975; Graciaa 1995). This negatively charged air-water interface provided an environment for clay colloid sorption which affinity was pH dependent (Wan 2002).

The understanding of the above stabilizing factors led to the decision of investigating the effect of magnetic stirring on the oil-water separation rate in this research.

According to Dunchan (2000) a high Newtonian viscosity will retard the rates of creaming, sedimentation, coalescence, etc'. Therefore, the rheological properties of the continuous phase will also influence the stability of an emulsion by influencing the possibility of two solid particles from approaching one another due to the difficulties in expulsing the continuous phase from between them. The viscosity of the continuous phase is one of the factors (Francis et al. 1995) and the presence of stabilizers such as gum will contribute to this too. The study on the effect of dilution on separation rate of the three phases may be able to prove the above discoveries.

2.3.3 Mechanisms of emulsion breaking

With the understanding of the factors for stable emulsions, it is important to understand the mechanisms and factors causing the emulsion breaking so that effective measures may be applied for pre-treatment of POME emulsion. Emulsion breaking is the process of getting the dispersed oil droplets to come together and form separate layers of oil and water. The mechanism of emulsion breaking involves the collision of the dispersed emulsion droplets, oil droplets in oil-water emulsion or solid particles in some colloid suspensions. The collision is accompanied by deformation (flattening in the zone of contact) to form a floc of droplets or bigger droplets. Figure 2.5 shows the three scenarios for the behavior of a two colliding oil droplets in an emulsion depending on the properties of the films (Ivanov and Kralchevsky 1997).

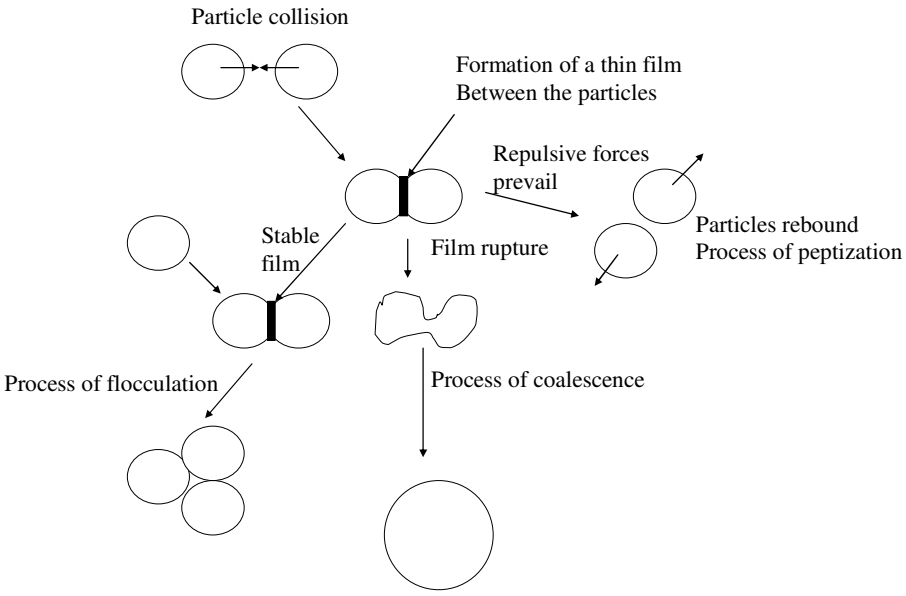


Figure 2.5: possible results of the collision of two emulsion droplets in connection with the droplet-droplet interaction (Ivanov and Kralchevsky 1997).

(1) In scenario one, when the film formed on particle collision is stable, flocks of attached particles can appear. This flocculation or clustering process results in closer aggregation of the dispersed droplets by Brownian motion and can lead to the destabilization of the emulsion. The floc may or may not separate out depending on its density. When the floc becomes large enough to be separated, sedimentation or creaming occurs due to the density difference between the two immiscible phases. The lighter phase tends to go up (creaming), whereas the heavier moves downward (sedimentation). In an oil-water emulsion, the oil drops accumulate at the top, forming a cream layer. The rate of this occurrence obeys Stokes law (Richardson and Harker 2003).

$$V_s = \frac{2r^2}{9}\frac{g(p_p - p_f)}{\eta} \qquad (2.2)$$

Where V_s = particles settling velocity

g = acceleration of gravity

ρ_p = density of the particles

ρ_f = density of the fluid

η = dynamic viscosity of the fluid

r = radius of the particles

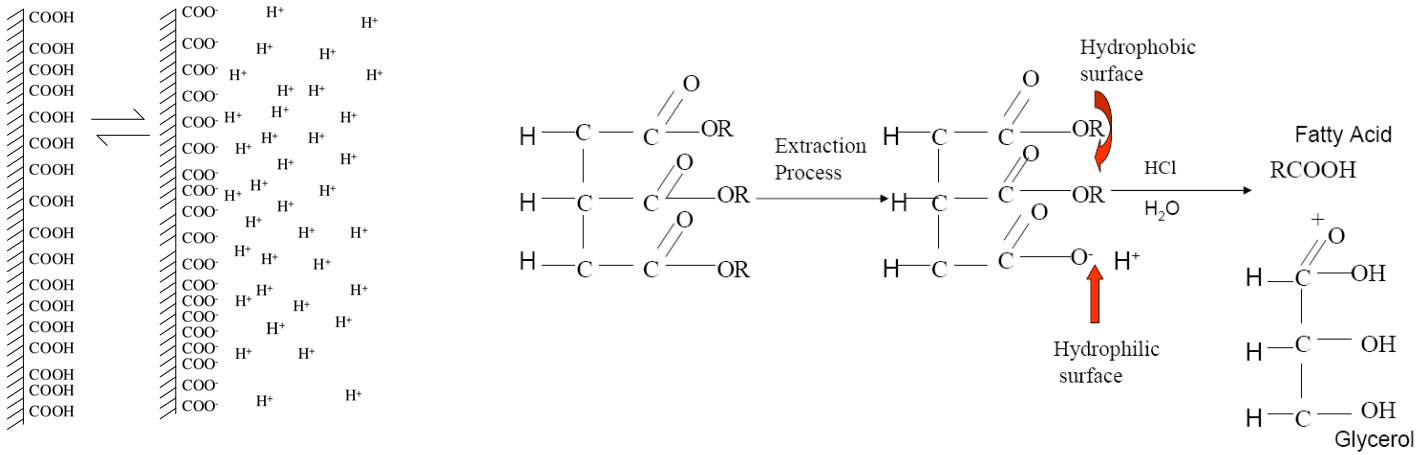
(2) When the attractive interaction across the film is predominant, the film is unstable and ruptures leading to the coalescence of the drops in emulsions or of the bubbles in foams. Therefore, flocculation is often a prerequisite step to coalescence.

(3) If the repulsive forces are predominant, the two colliding particles will rebound and the emulsion will be stable.

For a stabilized emulsion such as POME, emulsion breaking can be achieved through the addition of chemicals as shown in Table 2.2 and/or heat to the emulsified oil/water mixture. The most commonly used method of emulsion breaking is acid-cracking where sulfuric or hydrochloric acid is added to the oil-water mixture until the pH reaches 1 or 2. An alternative to acid cracking is chemical treatment using emulsion-breaking chemicals such as surfactants and coagulants. After addition of the treatment chemical, the tank contents are mixed. When the emulsion bond is broken, the oil residue is allowed to float to the top of the tank. At this point, heat (100 to 150 F) may be applied to speed up the separation process. The oil is then skimmed by mechanical means, or the water is decanted from the bottom of the tank. The oil residue is then further processed or disposed.

If chemicals such as mineral acids are used for oil-water emulsion cracking, the principles can be explained as the following figure 2.6.

The understanding of the emulsion breaking mechanisms leads to the decision of using HCl as an agent to provide positively charged cation for neutralization of the negative charges to enhance the coalescence of oil droplets for better separation rate. From the work done by Alther (2001)**,** HCl is a better mineral acid in facilitating the separation of oil and grease from emulsion and it is chemically less hazardous as compared to sulphuric acid.



(a) (b)

Figure 2.6: (a) the ionization of acid groups to give a negatively charged surface and neutralization by a positively charged cation (Everett 1988). (b) Reaction of HCl and water on the mechanically generated negative charges of the triglycerides to form hydrophobic fatty acids and hydrophilic glycerol.

2.3.4 Emulsion breaking (by chemical treatment)

To understand POME emulsion breaking, this section aims to review on previous research done on the separation of oil and solid from the combination of the three components which are oil, solid and water by chemical treatment, especially using HCl. The separation of oil by emulsion breaking through chemical treatment can be explained in Figure 2.6.

As shown in Figure 2.6, the oil contains acidic groups. The dissociation of its droplets due to mechanical agitation gives rise to a negatively charged surface. The magnitude of the surface depends on the acidic strength of the surface groups and on the pH of the solution. The surface charge can be reduced to zero by suppressing the surface ionization by decreasing pH. The cationic emulsion breaker such as HCl with positive charge produced by dissociation of HCl to H^+ can reduce the negative charged surface and converts the carboxyl ion in palm oil surface to carboxylic acid. This will reduce the repulsive electric charges and allow the oil droplets to collide, agglomerate and lead to a resolution of oil and water layer. Table 2.2 (Kemmer 1988) also shows a list of other chemical coagulating agents, such as salts of iron or Aluminum with Al^{3+}, $Fe^{2+/3+}$ after dissociation, that can be used in place of acid, with the additional benefit that these aid in agglomeration of the oil droplets. However, the Aluminum or iron forms hydroxide sludge that is difficult to dewater. Acids generally break emulsions more effectively than coagulant salts, but the resultant acidic wastewater must be neutralized after oil/water separation.

Alther (2001); Ang and Himawan (1994) had done studies that showed very successful use of acid cracking for grease recovery from oily wastewater. However, Alther (2001) used both hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) to break oil-water emulsions and found that HCl often seems to be superior.

Table 2.2 Common Chemicals used for Oily Wastewater Treatment (Kemmer 1988)

Main type	Description	Charge	Used for
Inorganic	Polyvalent metal salts such as alum, $AlCl_3$, $FeCl_3$, $Fe_2(SO_4)_3$	Cationic	O/W (Oil in water)
	Mineral acids such as H_2SO_4, HCl, HNO_3.	Cationic	O/W and W/O
	Adsorbents (adding solids) – pulverized clay, lime	None	O/W
Organic	Polyamines, polyacrylates and their substituted copolymers	Cationic	O/W
	Alkyl substituted benzene sulfonic acids and their salts.	Anionic	W/O (Water in oil)
	Alkyl phenolic resins, substituted polyalcohols	Nonionic	W/O

Ho and Tan (1983) reported that one of the components of solid in POME is sand which is silica. The study done by Pacek, (2007); Pichot, Spyropoulos and Norton (2009) on the effect of pH on the physical properties of the silica particles in the emulsion system showed that at pH > 4, the silica particles become highly charged which resulted in the dispersion of silica particles away from the oil-water interface and thus destabilizes the emulsion. At pH < 4, the silica particles are not charged and are therefore closely packed or forming multi-layers around the oil-water interface and therefore preventing oil droplets to coalesce. Yan (1996) reported the clay particles desorption from oil-water interface at pH higher than 6 and re-adsorption at pH lesser than 6 because of the deviation of contact angle from 90^0. From this review, the chemical treatment using HCl for POME emulsion breaking may not be effective in separating solids such as silica from the emulsion.

Another research done by Chow and Ho (2002) reported that the oil droplets extracted from POME consists of 84% neutral lipids and 16 wt% of complete lipids (6 wt% glycolipids and 10 wt% phospholipids). Chen et al, (2000); Comasa, Wagnerb and Tomas (2006); Wagner, Sorgentini and An˜ o´ n (1996) reported from their study on the influence of pH on different surfactants such as Lecithin which is phospholipids, that a pH lower than 2 will inhibit the emulsifying ability of the surfactants. Dekoning and McMullan (1965) had done the study on the hydrolysis of phospholipids by HCl into different compounds which can explain the above description of the change in surface activity of phospholipids when pH of the system is changed. The study done by Burczyk, (2002) on the effect of pH on the surface activity of the surfactant Triton SP-190 also agreed on the ability of acid in reducing the stabilization activity of the surfactant by surfactant hydrolysis. Apparently, when the hydrophobic part of the surfactant was chemically cleaved from the surfactant hydrophile in the presence of acid as reported by Union Carbide (1996), the interfacial properties of Triton SP-190 were affected, and its emulsification efficiency was greatly reduced. This review seems to explain the application of HCl to POME emulsion will enable a faster separation of solids from the emulsion because the emulsifying activities of the emulsifiers are destroyed at low pH.

The above review shows that the effect of low PH on the negative charges of oil produced mechanically in emulsion and the activities of surfactants in emulsion is just the opposite of the activities of silica particles in emulsions. This will serve as a very valuable guide for the analysis of the results obtained from the experimental work on the effect of HCl on oil and solid separation rate from POME in the following chapters of this research study.

2.3.5 Emulsion breaking (by heat treatment)

Another common method of enhancing POME emulsion breaking is by heat treatment. Several processes such as flotation and enhanced oil recovery occur at high temperatures. The solid-solution equilibrium of a system will also be significantly affected by changes in temperature and precipitation of various species due to temperature fluctuations that can markedly affect the interfacial potential (Ramachandran and Somasundaran 1986).

Stokes law, mentioned in 2.3.4 states that the rate of creaming and sedimentation can result from the action of gravitational force on phases that differ in density. This difference in density can be induced by the increase of temperature to the emulsion. Different phases respond to the same amount of heat applied at different rate because of the difference in specific heat capacity.

The specific heat capacity of palm oil is 2.0518 J/g/k (Morad et. al 2000) while the specific heat capacity of water is 4.186 J/g/k. So oil droplets will gain energy more quickly than the water molecules to counteract the repulsive force and coalesce with one another to form a separate layer normally on the surface. The viscosity and density of water decrease with an increase of temperature. This would lead to a greater difference in densities between water, oil and solid, which in turn would increase the solid settling rate and oil flotation rate according to Stokes law.

The phenomenon of increasing solid settling rates with the increase of temperature is also reported by Dunchan (2000) which states that a high Newtonian viscosity will retard the rates of creaming, sedimentation, coalescence, etc. The viscosity of water is a function of temperature. At higher temperature, the viscosity of water is lower. As the temperature increases, decreasing of water viscosity leads to a reduction of the shear stress between the water and solid particles which will then allow the solid particles to settle down more easily.

In emulsions stabilized by emulsifiers or surfactants, Flores et al, (2005) reported that many other factors such as PH, ionic strength and the type of emulsifiers present can affect the heat stability of the emulsion. The study done by Demetriades et al, (1997) had similar discovery. It was reported that certain emulsion breaking occurs at particular temperature range, but higher temperature may not necessarily increase oil droplets aggregation due to the mechanisms of inter-droplet and intra-droplet interaction which are favoured at different temperature range (Euston, Finnigan and Hirst 2000; Monahan et al. 1996; Sliwinski et al. 2003). The type and concentration of emulsifier or surfactant present will also determine the emulsion breaking response to heat treatment at different temperature range (Hunt and Dalgleish 1995; Josephine and Dalgleish 1995).

Chansiri et al. (1999) reported that autoclaving of an oil/water emulsion will cause hydrolysis of surfactants such as egg phospholipids to become fatty acids These acids create an acidic environment that will enhance the coalescence of oil droplets. The mechanisms of the occurrence could be similar to the case explained in Figure 2.6.

The review above shows that heat treatment at suitable temperature range at specific PH and ionic strength of a specific emulsion will lead to an increase in emulsion breaking rate of that particular oil-water emulsion. One of the investigations to be done in this research therefore aims at finding out the emulsion type of POME by examining its response to the heat treatment at different temperatures, acidic treatment and magnetic field treatment.

2.3.6 Emulsion breaking by magnetic stirring

Since electrostatic effect**,** as mentioned in section 2.3.3 is one of the emulsion stabilization factors, application of magnetic field on emulsion breaking has been used by many for treatment of water. The formation process of POME emulsion as described in section 2.3.1 implies that one of the stabilizing factors of POME emulsion is the electrostatic effect established by the negative charges formed around the oil droplets during mixing and pumping in tanks and centrifuges.

Magnets have the effect of repelling the water in the oil-water mixture, causing the oil droplets to collect at the area of the strongest magnetic field. The magnet is repelling the diamagnetic water, pushing it off to the sides (Forcefield. 2002). Water structural modifications induced by magnetic treatment have been endorsed by different scientific societies in Russia, United States, Belgium, Canada and others. The research has revealed the evidence that all structural changes of water dispersed systems treated by magnetic field have to do with the ions of substances present in the water, colloidal particles of considerable magnetic susceptibility and water changes. Magnetic treatment of water affects its wetting capacity of solid surfaces owing to changed interaction patterns of water molecules as it has been mentioned before. This “pushes” the water molecules off the surface (Marinova et. al. 1996). The benefits of water magnetic treatment also attribute to altered adsorption of individual ions on the surface. Therefore, the surface charge undergoes changes too. Improved wetting of hard surfaces after magnetic treatment of water enhances coagulation of suspended particles and increases aggregate instability of suspensions (Carruthers 1938; Wie and Fuerstenau 1974).

2.4 Framework of Research Study

From the current literature survey there was no documented study done on the chemical characteristics of POME as an emulsion and its response to chemical and physical treatment such as addition of HCl, temperature change, magnetic stirring and dilution. There is also little information on the composition and interactions of the three

components, namely oil, solid and water of POME. Most of the previous research work focused on the physical treatment at the secondary treatment stage and biological treatment on the primary treatment. There was no detailed study done on the combined chemical and physical treatment before the primary treatment stage, that is, treatment at the de-oiling stage as shown in Fig 2.1. Due to the low content of oil and usually thick brownish slurry in the raw POME, this makes it difficult to carry out the experimental observation on the rate of oil and solid separation. Therefore, different synthetic mixtures of the 3 components of POME (oil, solid and water) will be used for the purpose of experimental study in this research. The different mixtures are palm oil-water mixture, decanter solid-palm oil mixture, decanter solid-water mixture and palm oil-solid-water mixture or clarifier sludge-water mixture. The pre-treatment stage in Figure 2.7 will be the focus of this research studies.

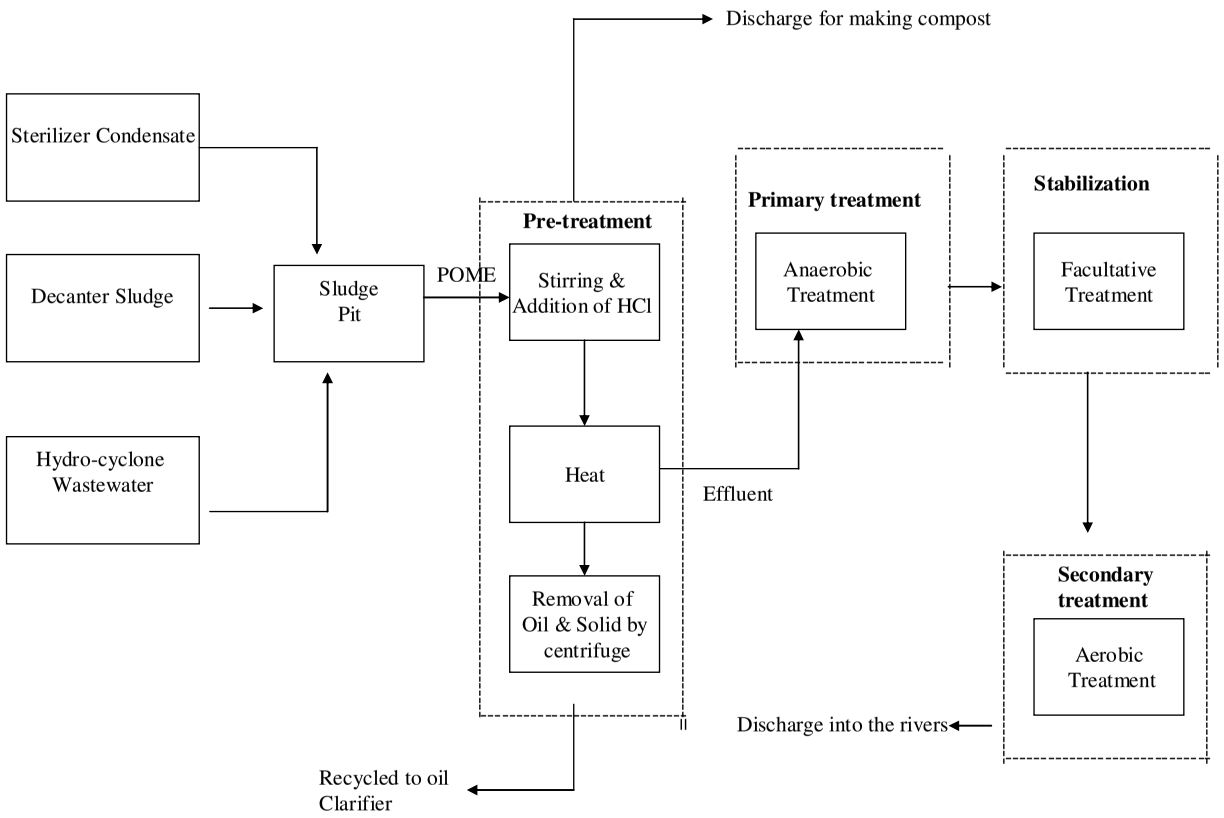


Figure 2.7: Stages of POME treatment Processing units

Chapter 3

Rate of Oil Flotation

3.1 Introduction

Palm oil mill effluent (POME) is made up of the three major components which namely oil (0.9-1.5%), solid (5-7%) and water (93-95%). It exists as a layer of free oil on the surface, settled solid in the bottom and a middle layer with the suspended solid-oil-water emulsion. The free oil can be easily skimmed off and the settled solids removed, but the suspended solid-oil-water layer, which could not be removed mechanically, remains as a problem.

The resulting high BOD of POME and hence the long hydraulic retention time (HRT) of 120 – 200 days required in the current treatment system of POME, is not environmentally friendly because a huge amount of water would be trapped and unused for a long period of time. It would also be a loss of revenue for the palm oil mills for the large amount of oil to be degraded and discharged. One reason for the long HRT is the long chain fatty acid present in the oil that inhibits the anaerobic microbial degradation of the organic matter in POME (Hanaki, Matsuo and Nagase 1981; Koster and Camer 1987). It is not surprising that the present line of strategy adopted to treat the liquid waste is to remove as much oil as possible from the crude POME at the pre-treatment stage.

A number of methods have been studied to remove the oil residue in POME as described in Section 2.2.3, but they were only operational at laboratory scale because of the limitations in each individual method. Most of the methods could only treat POME after

the pre-treatment and anaerobic stage where the solid content had been greatly reduced. This showed that the high solid content in POME could be a hindrance to speedy oil removal.

As described in Section 2.3.3, studies had also been done on the separation behaviour of oil from oily wastewater or oily emulsion rather than POME as demonstrated by Ivanov and Kralchevsky (1997); Everett (1988); Kemmer (1988); Ang and Himawan (1994) and Alther (2001). All the later three researchers recommended the use of mineral acids, especially HCl, as a chemical treatment to enhance oil separation rate. Stokes law and differences in specific heat capacity of the three different components could explain clearly the predicted positive effect of heat on the rate of oil separation from a stabilized oil-water mixture. Forcefield (2002); Marinova et al (1996); Carruthers (1938); Wie and Fuerstenau (1974) had studied on the possibility of applying magnetic field for separation of charged oil particles from oil-water mixture stabilized by electrostatic effect.

The separation behaviour and the interaction of each component, oil or solid or water in the emulsion layer of POME had not been well studied and documented. It would be difficult to do such investigations with the raw POME with its high concentration of dark coloured solid of different type, shape and size and the oil droplets being trapped within. At this stage, synthetic mixtures of POME were designed by assuming the solid had been completely removed either chemically or mechanically. The study focussed on the investigation of the rate of oil flotation from crude palm oil-water and refined palm oil-water mixtures at different determined ratios under the determined treatment conditions.

In this Chapter**,** the respective effect of hydrochloric acid (HCl), heat and magnetic stirring on the rate of flotation of crude and refined palm oil from the mechanically mixed oil-water emulsion was investigated. Statistical analysis and kinetic modelling were also carried out to establish the significance of the variables studied and the relationships between the parameters involved. To date, no systematic studies on the

kinetics of the crude and refined palm oil separation in the presence of acids, heat treatment and magnetic field had been reported. The kinetic data would provide valuable information on the effectiveness of the above methods and their application potential in the pre-treatment of POME.

3.2 Problem Formulation and Approach

As described in the introduction, the suspended solids in POME are the main cause to the treatment difficulties. The POME mixture was formed by vigorous pumping and flushing during the crude palm oil extraction process. It formed a stable emulsion as described in Section 2.3.2. The stability could be caused by the negative charges of oil droplets generated mechanically during pumping and flushing and could be explained by Derjaguin, Landau, and Verwey and Overbeek (DLVO) theory.

The other possible reasons could be attributed to its chemical complexity and heterogeneity of POME.. The presence of different glycerides and lipids especially phospholipids in the solids and oil could be acting as stabilizer of POME emulsion (Chow and Ho 2002). The solid of different types, shapes and sizes could form a coating layer around the dispersed oil droplets to prevent coalescence of oil.

In order to enhance a more efficient treatment process, the breaking of the stable POME emulsion becomes an important issue to tackle. The challenge to address this problem becomes the motivation of this research study. However, the high concentration of dark coloured solids of difference sizes and shapes, and the trapped oil droplets, separation behaviour and the interaction of each component (oil, solid and water) from the raw POME made the investigations on the emulsion breaking very difficult. To mitigate such difficulties, the synthetic mixtures of the 2 components at different ratio combinations were specially devised in the initial study. The mixtures devised for investigations were palm oil-water mixtures and refined palm oil-mixtures. Refined palm oil (RPO) was palm oil that was refined, bleached and de-odorized so that phospholipids, β-carotene and free fatty acids were removed by treatment of phosphoric acid and distillation under high temperature (De Greyt and Kellens 2000). The study of its flotation and separation

behavior under the same treatment conditions as palm oil-water mixtures would give insights to the stabilizing function of the phospholipids, β-carotene and free fatty acids in palm oil-water mixtures.

The investigation of the rate of oil separation from synthetic palm oil-water mixtures and refined palm oil-water mixtures of different ratios was carried out by assuming that solid had been completely removed. Such study would enable a better understanding of the separation behaviour and interaction of palm oil and water under the designed treatment conditions without considering the complex effect of the solid. It would later lead to the understanding of palm oil separation behaviour in POME where solid co-exists with palm oil and water. The use of synthetic oil-water mixtures for this study also enabled an easier measurement of the rate of oil flotation without purchasing sophisticated, expensive equipments such as turbidimeter (Welz, Baloyi and Deglon 2007) or spectrophotometer.

The rate of oil flotation was the key parameter to measure the extent of oil separation. It was a measure of the volume of oil (ml) disengaged from the oil-water mixture to float to the surface at every fixed time interval (Al-Zuhair 2004). The initial stage of this research was to artificially create a palm oil-water mixture of different ratios such as 45:55, 40:60 and 30:70 for the study of oil flotation rate under different conditions which had long been established as factors affecting rate of oil separation from oily water or emulsion. These conditions were treatment with HCl of different concentrations, heat at different temperatures, application of magnetic stirring and different oil concentrations. However, the oil-water emulsion devised in this study cannot be used to fully represent POME for the study of rate of oil flotation. POME contained oil, solid and water. The oil content was only 0.9 – 1.5% and therefore comparatively lower than the concentration of oil in water used in this study. It was impossible to study the rate of oil flotation with such low oil concentration due to lack of very high speed mixer and also no solid content. The behavior of solid with oil and water would not be known in this study. Therefore, the separation and interaction behavior of solid in POME would be studied in the next two Chapters by using solid-

palm oil mixture, solid-water mixture and oil-solid-water mixture. The following two chapters would provide a more holistic understanding of the separation behavior and interaction of all components in POME under the same treatment conditions.

3.3 Materials and Experimental Methods

3.3.1 Materials

Crude Palm Oil

The crude palm oil used in our experiments was collected from the output of the clarification unit before being transferred to the storage tanks at the BLD mill. The samples for the tests were made up of a mixture of the crude palm oil with water in a ratio of 45:55, 40:60, 30:70, and 20:80 (v/v%). It is used for the study because this is the same type of oil present in the POME.

Refined Palm Oil

The refined palm oil or the refined bleached deodorized palm oil (RBDPO) is the product of Lam Soon, branded KNIFE. The same test was carried out with RBDPO to obtain better understanding to the factors affecting the rate of oil flotation. The samples for the tests were made up of a mixture of the refined palm oil with water in a ratio of 45:55 by volume.

Hydrochloric Acid (HCl)

With the understanding from the literature review in chapter 2, acid cracking is one of the chosen methods for the study of oil and solid separation from POME in this research and a commercial grade Hydrochloric acid (HCl) was used as the reagent for the following reasons:

It is one of the least hazardous strong acids to handle that produces less reactive and non-toxic chloride ion. It is quite stable, maintaining their concentrations over time. These attributes therefore serves as the motivation in using HCl to be the chemical as emulsion breaker in this research, instead of H_2SO_4, which is comparatively cheaper. The concentration of HCl to be added to oil-water mixture was as follows:

0.5 and 1.0 (v/v%).

Equipments and Apparatus

- Hot plates (Figure 3:1) – to provide heat to the water bath used for heating of oil-water mixtures.
- Magnetic stirring bar – It was used together with a combined hot-plate magnetic-stirrer device (Figure 3:1). The left knob controls the stirring rate and the right knob controls heating. It was used at the experiment for testing the effect of magnetic stirring on rate of oil flotation.

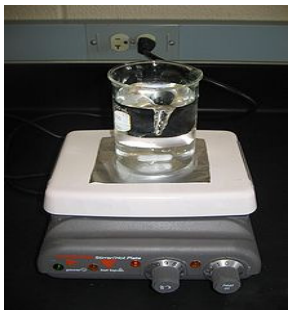


Figure 3.1: A combined hot-plate magnetic-stirrer device

Measurement Methods for Rate of Oil Flotation

The rate of oil flotation was determined by reading off the increase in volume of oil (ml) disengaged from the mixture to float on the surface of the graduated measuring cylinder as shown in figure 3.2, at every 1 minute time interval (Al-Zuhair 2004). The duration of the separating process was determined by the leveling off point of the flotation curve where no more volume change of oil can be observed physically. Five runs were carried out for every same test to eliminate statistical error and an average of the five sets of data was used to establish the flotation curve. The initial readings before the leveling off point of the flotation curve were used for establishing the kinetic model. Errors might arise in this experimental method due to the inconsistencies during the separation process. Some water might be trapped in between two layers of oil either horizontally or vertically that made reading of volume change difficult. An estimate had to be made in such cases. Another estimate had to be made when a big bulk of oil rising at fast speed and the volume might not align with the graduation scale of the measuring cylinder.

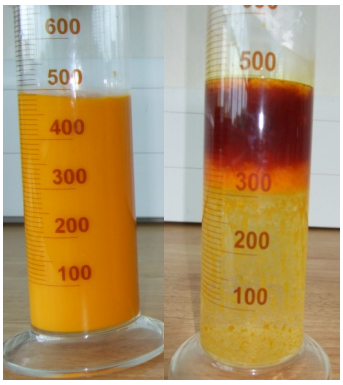


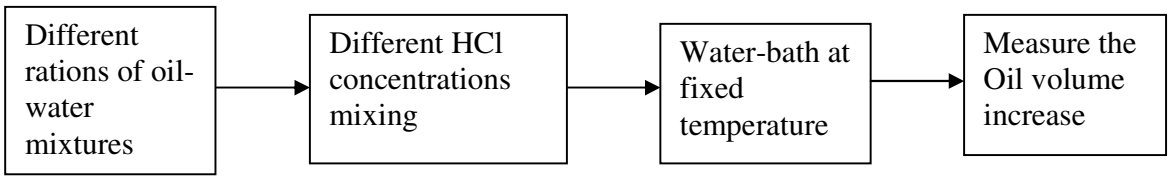
Figure 3.2: Measurement of oil flotation rate

3.3.2a Experimental methods for Crude palm oil-water mixture

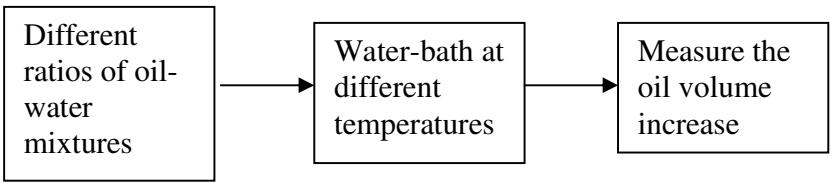
General Experimental Procedure

The flow charts below show a general experimental procedure as described in Section 3.3.2a and 3.3.2b

For investigation of HCl effect



For investigation of heating effect



For investigation of magnetic stirring effect

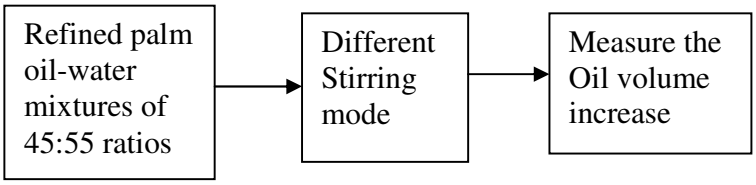


Figure 3.3 Flow chart of general experimental procedure

Treatment with heat

The tests were carried out to determine the rate of oil separation by establishing a flotation curve on the increasing volume of clarified oil (ml) with every minute time interval. A graduated glass cylinders of 100ml was placed in each of the controlled water-bath at a fixed temperature in the range of 75^0C to 95^0C and filled with preheated samples of crude palm oil-water of a specified ratio. The change of the volume of clarified oil with time was recorded.

Five runs were carried out for each heating temperature. Statistical analysis (e.g. least squared fitting) was performed on the collected data to determine the separation rate without additional treatment.

Another five runs of scale-up experiments were performed by using graduated glass cylinders filled with 500ml of desired ratio of crude palm oil-water mixtures of 30:70 or 40:60 and place them into a temperature controlled water-bath tank that were filled with 15 gallons of 70^0C water. The changes of the volume of clarified oil with time were recorded. Statistical analysis was performed on the collected data to determine the separation rate with temperature treatment. The tests were repeated by setting the water-bath temperature to 80^0C and 90^0C.

Treatment with HCl

The experimental procedure for this part of the study is similar to the procedure used for heat treatment except for the addition of HCl of different concentration for different tests.

Treatment with magnetic field and stirring

The same procedure was carried out five times for the samples treated with magnetic stirring, magnetic field without stirring and without magnetic field & no stirring at a fixed room temperature and oil-water ratio (45:55). These experiments were performed to examine the effect of different stirring conditions on the separation rate.

3.3.2b Experimental methods for Refined Palm Oil-Water Mixture

Those experiments in section 3.3.2a were not only performed on the crude palm-oil-water mixture, but also on the refined palm oil-water mixture. Only a 45:55 refined oil-water mixture was used to test on the effect of 0% and 1% HCl on the separation rate at the temperatures of 75^0C, 85^0C and 95^0C. Only 100ml samples were used for the determination of oil flotation rate.

3.4 Results and Discussion

The results obtained in the study of this chapter are presented and discussed in the following sections:

3.4.1 Treatment with HCl

Figures 3.4 shows the results obtained from tests done on effect of treatment with and without HCl under a fixed temperature of 95^0C and an oil-water ratio of 45:55 in 100 ml palm oil-water mixtures.

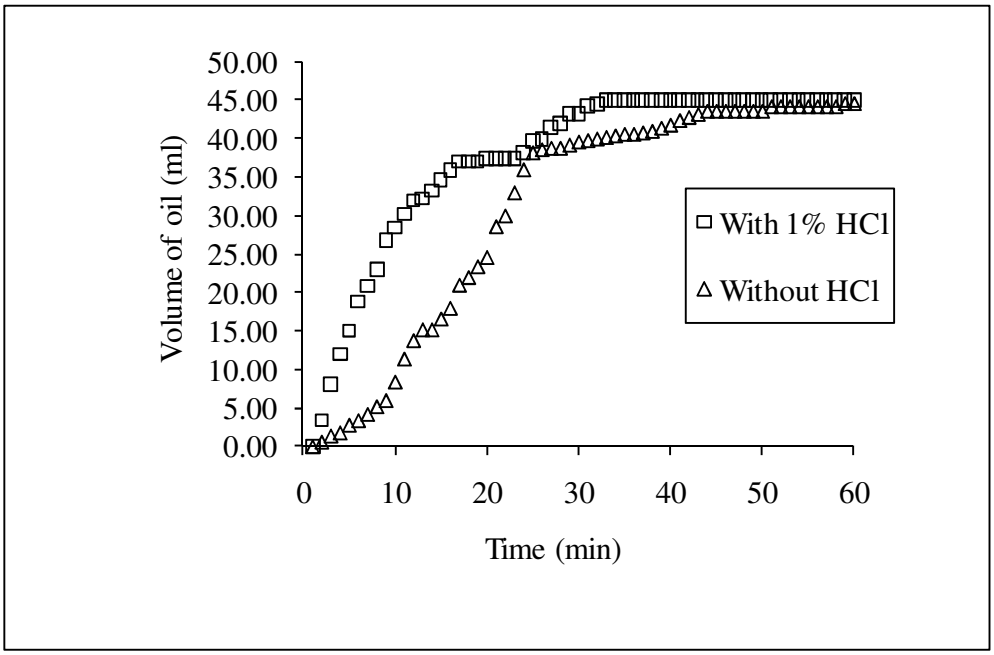


Figure 3.4 Treatments with and without 1% HCl at 95^0C for 45:55 Crude palm oil-water mixtures in 100ml sample.

The results showed that treatment of palm oil-water mixtures with 1% HCl significantly increased the rate of oil flotation. Figure 3.5 also shows a significant increase in rate of oil flotation when the 100 ml of 45:55 refined palm oil-water mixture was treated with 1% HCl at 75^0C. The oil flotation rate in refined palm-water mixture was so fast that only 75^0C was selected for the test.

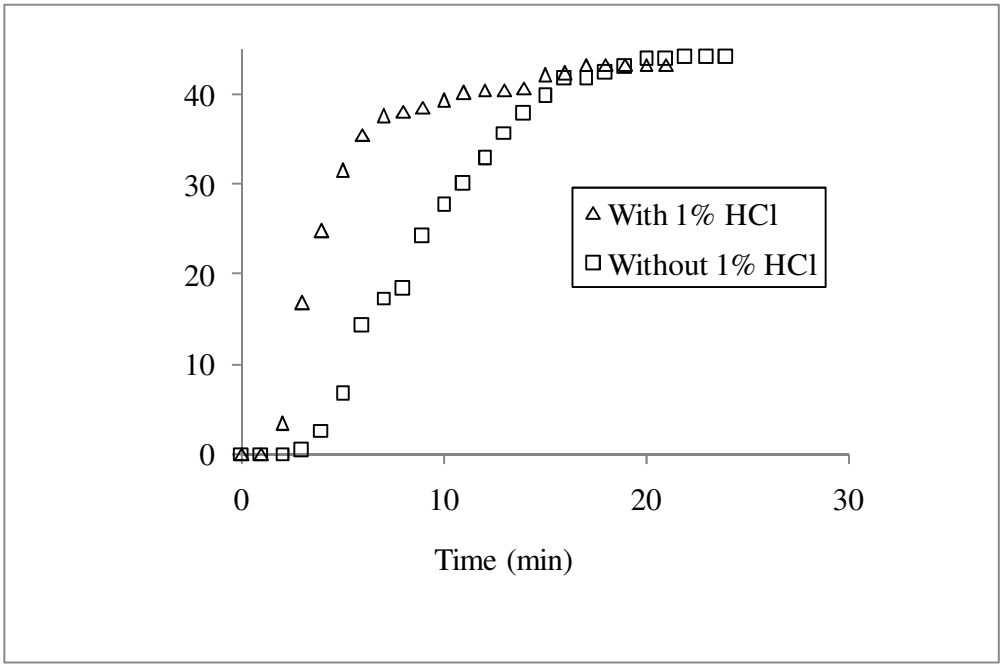


Figure 3.5 Volume of Refined Palm Oil (ml) with time (min) with and without 1 % HCl at 75^0C for 45:55 refined palm oil-water mixtures in 100ml sample.

A data analysis done by using kinetic models described in appendix A provided a more quantitative description of the positive effect of HCl shown in Tables 3.1 and 3.2 below.

Table 3.1 Kinetic parameters for palm oil floatation rate with treatment and without treatment of HCl at 95^oC

Treatment	*k*	*N*
With HCl	0.020	0.065
Without HCl	0.015	0.055

Table 3.1 shows the effect of treatment with hydrochloric acid (HCl) on the crude palm oil floatation rate. The value of *k (kinetic rate)* for treatment with HCl is approximately 30% higher than that without treatment. This indicates that the HCl treatment has a significant improvement on the rate of floatation.

Table 3.2 Kinetic parameters for refined palm oil with treatment and without treatment of HCl at 95^{o}C

Treatment	*k*	*N*
With HCl	0.077	0.092
Without HCl	0.030	0.042

Table 3.2 shows that the HCl treatment also greatly increases the oil flotation rate in the refined palm oil by 150%. The comparison between table 3.1 and table 3.2 shows that the HCl treatment has stronger impact on the refined palm oil than the crude palm oil. The *k* value for refined palm oil –water mixtures is twice as high as that of crude palm oil-water mixtures. This confirms the observation of a faster oil flotation rate in refined palm oil-water mixtures.

The above results agree with the prediction by Everett (1988) as shown in Figure 2.6 of Chapter 2 that the cation contributed by HCl could have neutralized the negatively charged oil droplets to enhance agglomeration and coalescence of oil droplets and speed up the rate of oil flotation. The low PH condition created by addition of HCl could have inhibited the emulsifying activity of the stabilizers or surfactants such as phospholipids present in the oil as reported by Chen et al, (2000); Comasa, Wagnerb and Tomas (2006); Wagner, Sorgentini and An˜ o´ n, (1996).

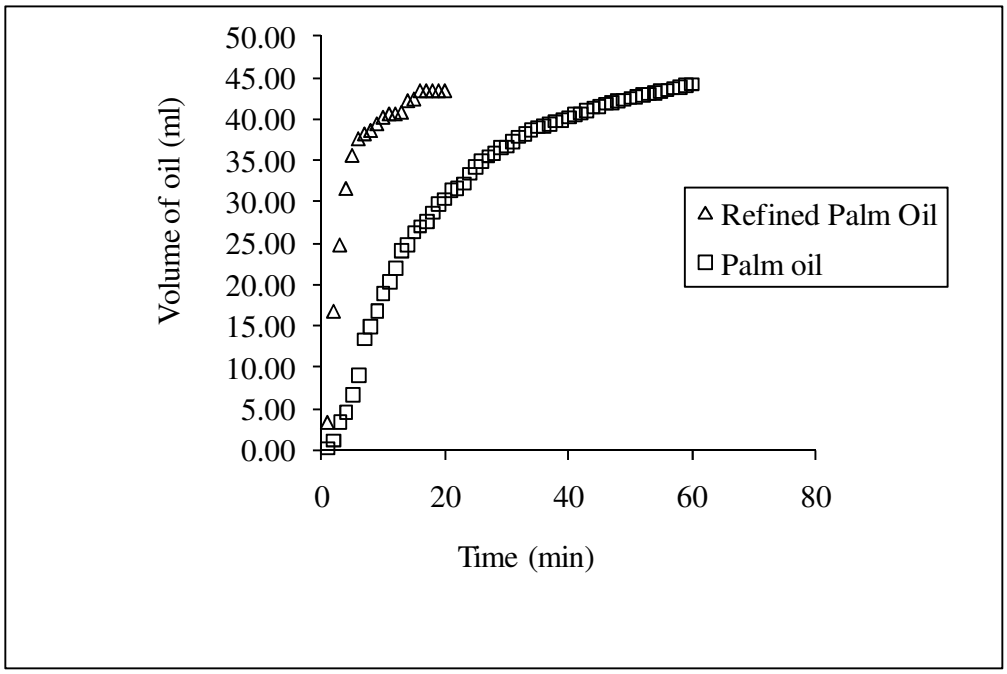


Figure 3.6 the differences in rate of floatation of oil between Palm Oil and Refined Palm Oil with 1% HCl at 75^0C for 45:55 oil-water mixtures in 100ml sample.

There are reasons for the rate of oil separation/flotation in refined palm oil-water mixtures to be so much faster as compared to palm oil-water mixtures of the same ratio treated with the same concentration, (1%) of HCl shown in Figure 3.6. The refined palm oil is the bleached and deodorized palm oil (RBDPO). The orange color which is normally the β-carotene has been removed and de-gumming removed phospholipids (De Greyt and Kellens 2000) which often acted as surfactants or emulsifier. The differences in the chemical content could be the reasons for their differences in reaction towards the same treatment of HCl shown in Figure 3.6 above and the more interesting results in Figure 3.7 below.

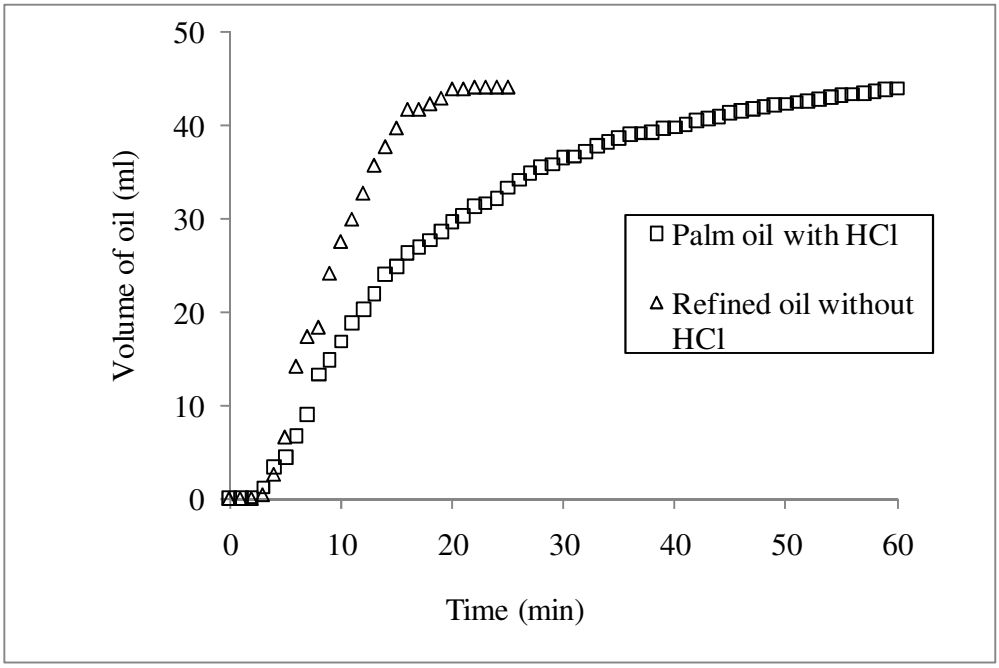


Figure 3.7 the difference in rate of floatation of oil between Palm Oil (with1% HCl) and Refined Palm Oil (without 1% HCl) at 75^0C for 45:55 refined palm oil-water mixtures in 100ml sample.

The results presented in Figure 3.8 showed significant increase in the oil separation rate in crude palm oil-water mixture of ratio of 30:70 treated with an increased concentration of HCl. However, a different scenario is shown in the results presented in Figures 3.9 and 3.10. No significant positive effect of the treatment with an increased HCl concentration is shown in the mixtures with ratios of 45:55 and 40:60. This phenomenon could be further confirmed by the data analysis done by kinetic modeling which showed in Table 3.1 that the value of *n (concentration of oil)* for HCl treatment is about 18% higher than that without treatment. Hence this implies that HCl tends to make the flotation rate more dependent on the oil concentration inside the oil-water emulsion (Pal and Masliyah 1990). The causes might be the mechanism of the reaction between HCl and those components present in crude palm oil which was dependant on the concentration ratio of each reactant.

However, more tests of a wider concentration range of both HCl and palm oil-water mixture need to be done to confirm the above observation. More tests and analysis may

be required to understand the chemical reactions between the carbonyl ions of the oil, the water molecules and the HCl molecules in order to know the reasons for the dependency of HCl treatment on the concentrations of oil in oil-water mixtures.

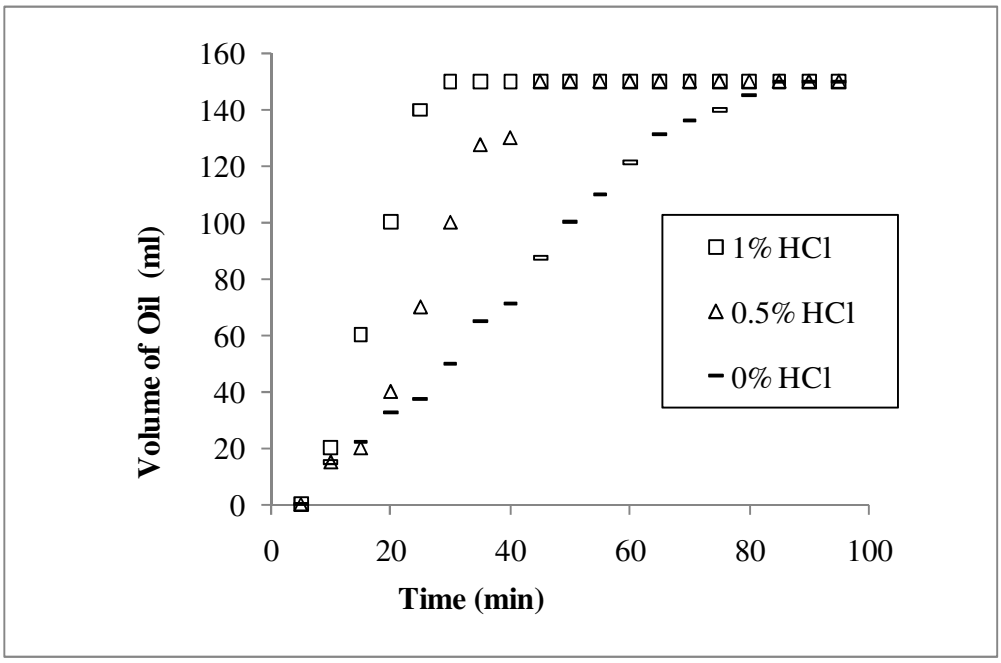


Figure 3.8 the treatment with 0% to 1% HCl at 90^0C for 30:70 Crude palm oil-water mixtures in 500ml sample

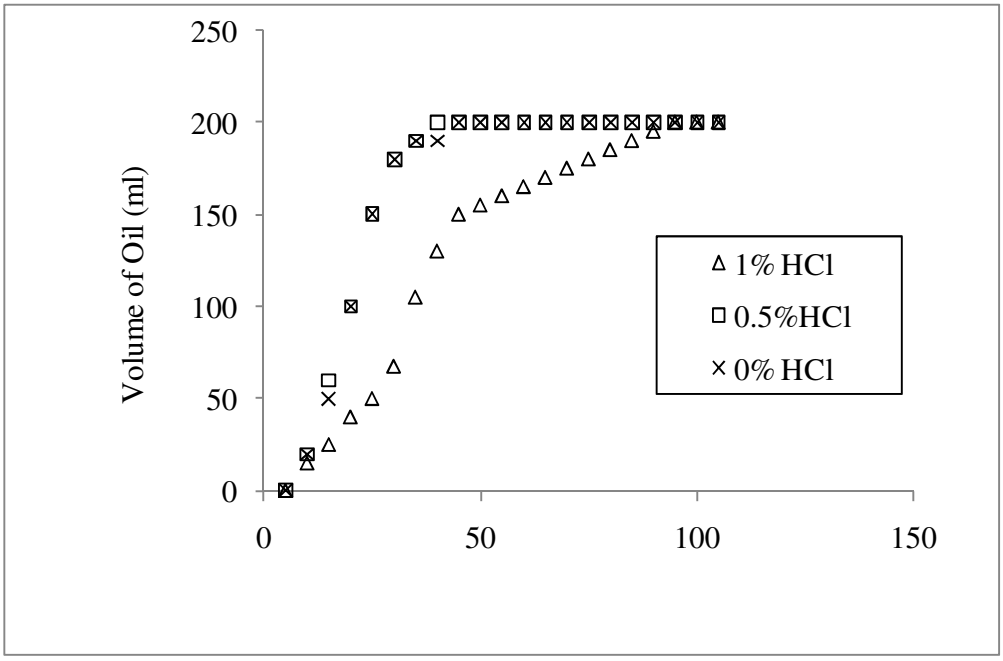


Figure 3.9 the treatment with 0% to 1% HCl at 90^0C for 40:60 Crude palm oil-water mixtures in 500ml sample

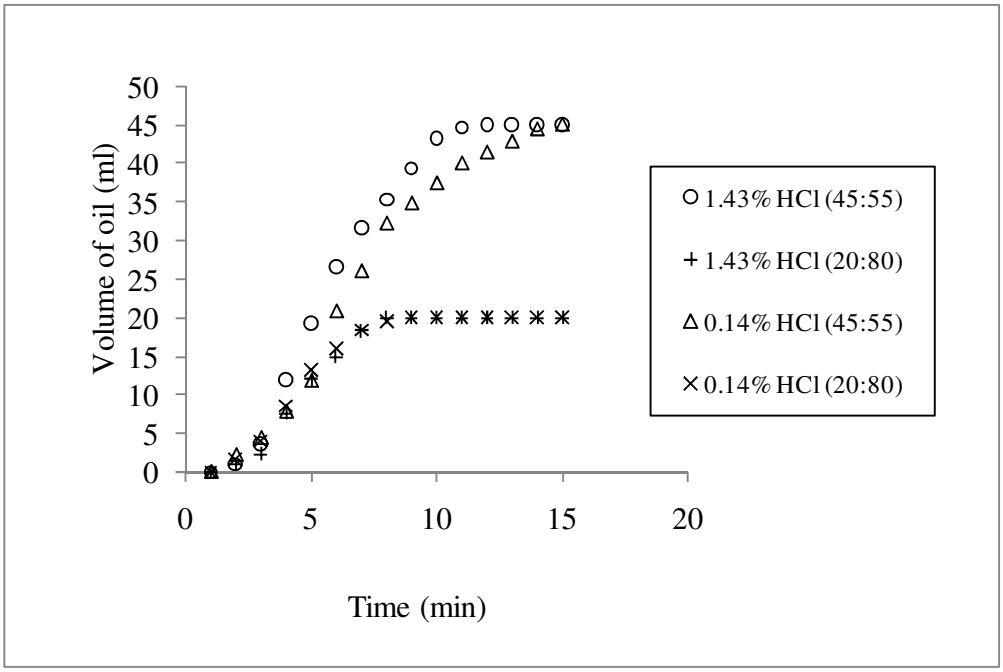


Figure 3.10 Palm Oil (ml) with time (min) at 90^0C for 45:55 Crude palm oil-water mixtures of 100ml sample.

On the other hand, the kinetic of refined palm oil shows less dependent on the oil concentration inside the oil-water emulsion (without HCl). The opposite effect is observed when HCl treatment is involved (refer to Tables 3.1 and 3.2) where the n value for refined palm oil is about 1.4 times as high as crude palm oil.

3.4.2 Treatment with Heat

Figure 3.11 below were results obtained from tests done on the application of heat to palm oil-water mixtures of ratio 45:55 at temperatures of 75^0C, 85^0C and 95^0C. The effect of heat treatment by increasing temperature on the crude palm oil-water mixtures of different ratios is found to be in line with the theoretical prediction by Stokes law which infers that the creation of a greater difference in densities and viscosities of the oil and water phases by the increase in temperature will lead to an increase in oil flotation rate (Richardson and Harker 2003). The difference in specific heat capacity of palm oil, 2.0518 J/g/k (Morad et. al. 2000) and water, 4.186 J/g/k will also lead to an increase in oil flotation rate because the particles of each phase will gain higher energy for collision and coalesce at different rate. A different set of results presented in Figures 3.12 clearly confirmed this fact. No quantitative comparison of oil flotation rate between samples of 500ml and 100ml treated under the same conditions were done in this study. Such quantitative comparison may provide insights to the effect of container size on oil flotation rate. Results from similar tests done by using refined palm oil-water mixtures of 45:55 at different temperatures again testify the positive effect of heat on oil flotation rate (Figure 3.13).

A data analysis done by using kinetic models described in appendix A is also developed for a more quantitative description of the positive effect of heat as shown in Tables 3.3.

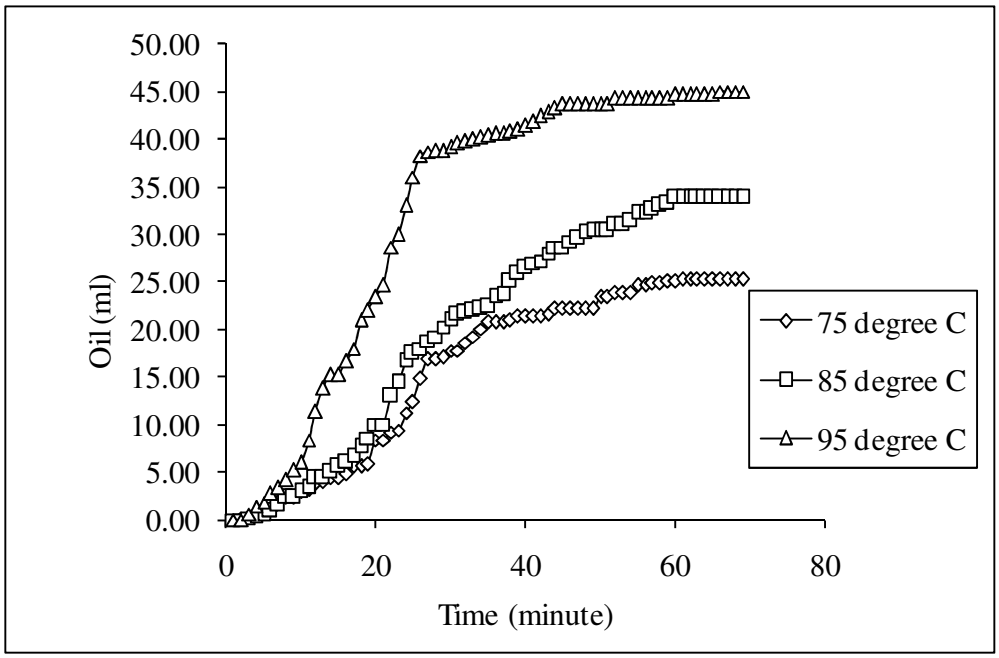


Figure 3.11 the volume of Palm Oil (ml) floatation to the surface with time (min) at different temperatures for 45:55 Crude palm oil-water mixtures in 100ml sample.

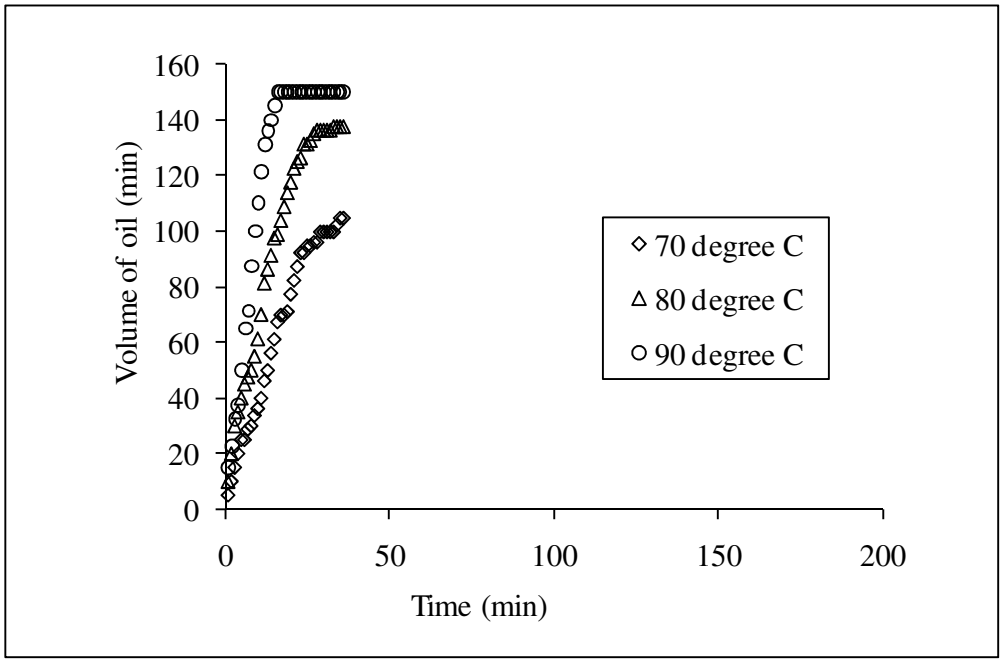


Figure 3.12: Volume of Palm Oil (ml) floatation to the surface with time (min) at different temperatures for 30:70 Crude palm oil-water mixtures in 500ml sample.

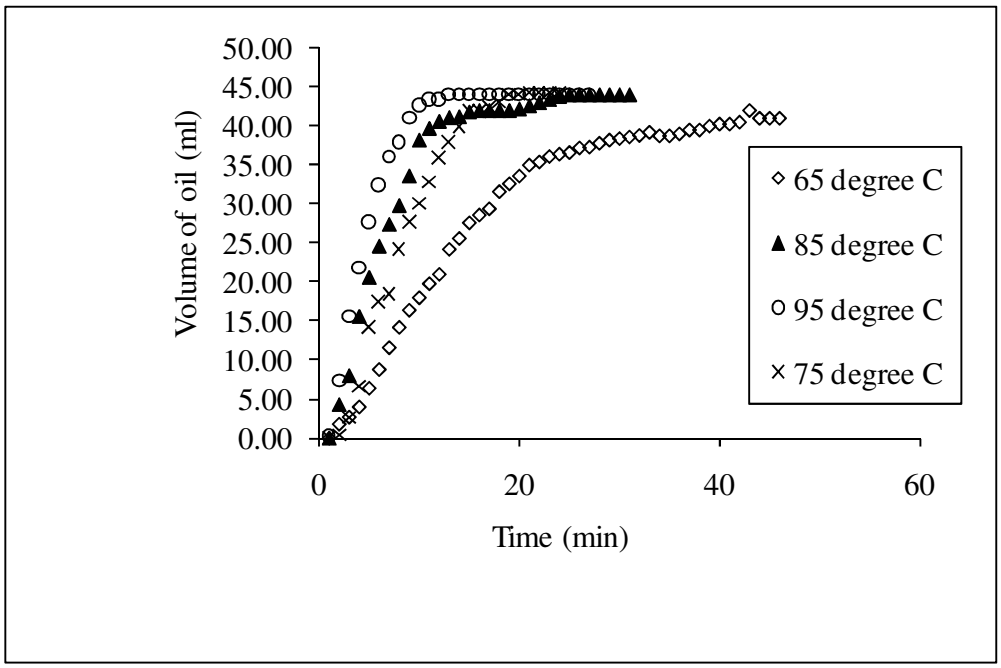


Figure 3.13 rate of flotation of oil in Refine palm oil-water mixtures of 45:55 ratios treated with different heat temperatures.

Table 3.3 Kinetic parameters for crude palm oil at different temperatures

Temperature	*k*	*N*
75^0C	0.006	0.101
85^0C	0.007	0.096
95^0C	0.014	0.052

Table 3.3 confirms the long standing observation in industrial practice that increasing the temperature of the oil-water emulsion can increase the rate of oil flotation. The k value increases about 130% from 0.006 to 0.014 when the temperature increases from 75^0C to 95^0C. This clearly shows a faster floatation rate at higher temperature. Also, increasing the temperature will decrease the dependent of floatation kinetic on the oil concentration shown by the decrease in n value from 75^0C to 95^0C.

(Chansiri et al. 1999) reported that autoclaving/heating of an oil/water emulsion will cause hydrolysis of surfactants such as egg phospholipids to become fatty acids. These acids create an acidic environment that will enhance the coalescence of oil droplets. The mechanisms of the occurrence could be similar to the case explained in Figure 2.6 by Everett (1988). This explanation was also in agreement with the experimental findings

from the effect of treatment with HCl on palm oil-water mixtures done in the earlier section of this chapter.

Table 3.4 shows a quantitative comparison of the difference in the rate of oil separation from crude palm oil-water and refined palm oil-water mixtures of the same ratio 45:55 at a fixed temperature of 95^0C.

Table 3.4 Kinetic parameters for refined palm oil and crude palm oil at 95^oC

Oil type	*k*	*N*
Refined palm oil	0.047	0.042
Crude palm oil	0.014	0.053

From Table 3.4, at 95^oC without HCl treatment the k value for refined palm oil is about 3 times that of the crude palm oil.

3.4.3 Treatment with Dilution

While investigating the effect of HCl and heat treatment on different combination of palm oil-water mixtures, the effect of palm oil-water ratios was discovered to play an important role in the rate of oil flotation too. This phenomenon was clearly shown in the results as displayed in Figures 3.14 and 3.15.

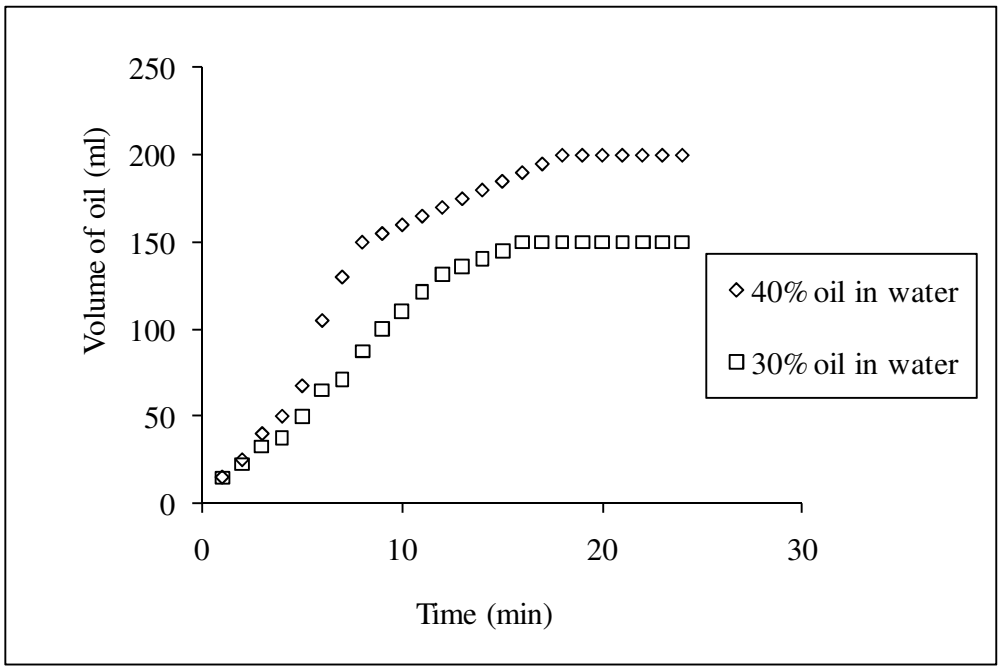


Figure 3.14: Volume of Palm Oil (ml) flotation to the surface with time (min) at fixed temperature (90^0C) for Crude palm oil-water mixture of different ratios in 500ml sample

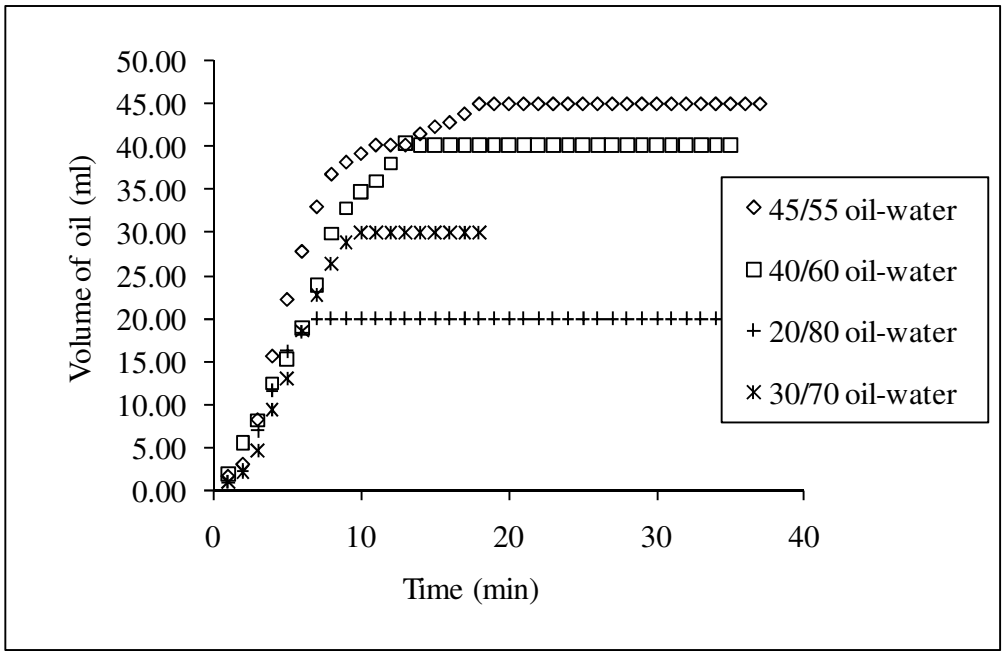


Figure 3.15 Effect of different Oil-water Concentration with treatment of 1% concentration of HCl at constant temperature of 85^oC in 100ml sample.

The higher frequency of collision between oil droplets due to its higher concentration could be the main cause of higher rate of flocculation and coalescence as explained by Ivanov and Kralchevsky (1997) in Figure 2.4. However, treatment with water dilution is not permitted by the Department of Environment in Malaysia. The method is therefore only feasible for study purposes.

3.4.5 Treatment with Magnetic Stirring

The trend of the separation process in the crude palm oil-water emulsion treated with magnetic stirring was shown in Figure 3.16 for three cases: (1) stirred with magnetic bar, (2) unstirred with magnetic bar and (3) unstirred without magnetic bar. The result showed that the emulsion stirred with a magnetic bar had a slightly higher separation rate than the emulsion with a magnetic bar with no stirring. The emulsion with no magnetic bar but with manual stirring applied had the slowest separation rate. However, the differences in the rate of oil separation and floatation were not large. The emulsion with no stirring and with no magnet appears to have slightly higher separation than either manual stirring without magnet, or no stirring with magnet. These counter-intuitive phenomena could be caused by inconsistencies in the stirring speed. The speed of manual stirring is different from stirring by magnetic bar. More studies have to be conducted with a stronger magnetic field applied to the emulsion in order to confirm the effect of magnetic field and stirring. The observations above on the separation behaviour of refined palm oil from its oil-water mixture in response to magnetic stirring appeared to be in agreement with Carruthers (1938) in section 2.3.3 about the presence of electrostatic effect between oil droplets and water. The slightly higher separation rate of oil from its oil-water mixture stirred with a magnetic bar could be a result of the repelling effect of magnets on water molecules in oil-water mixture.

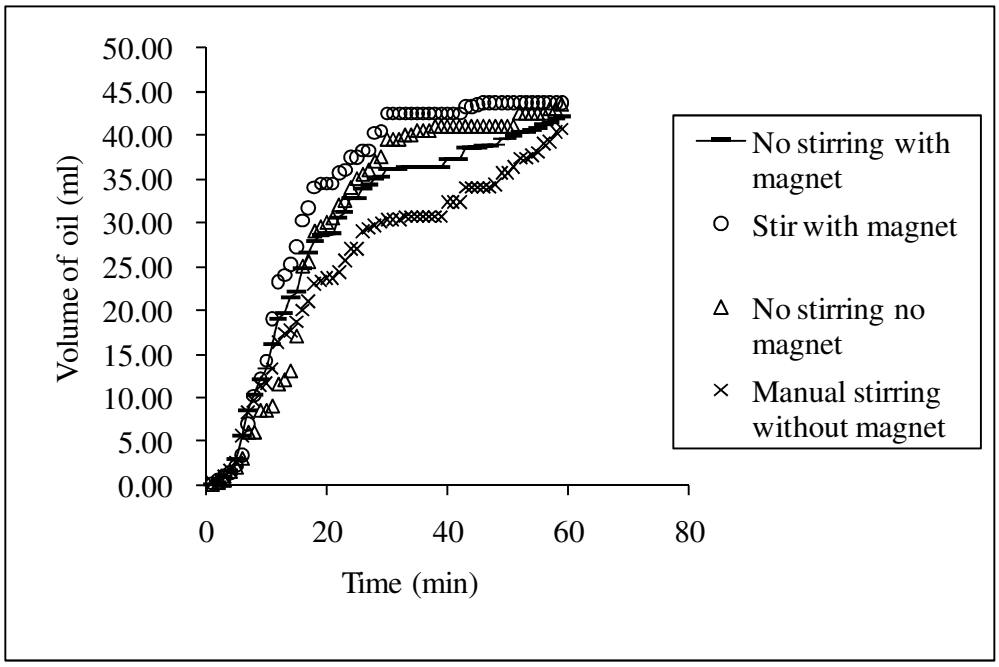


Figure 3.16: Volume of Refined Palm Oil (ml) floatation to the surface with time (min) at different stirring mode for 45:55 refined palm oil-water mixtures in 100ml sample.

Unlike the effects of temperature and HCl treatments, the effect of stirring is less pronounced. Table 3.5 shows the effects of stirring modes and magnetism. The *k* value resulted from magnetic stirring is about 40% higher than that with manual stirring. This could be due to not only more uniform mixing by magnetic stirrer but also by the magnetism effect. Although the *k* values are not strongly affected by magnetism but the *n* values increase by approximately 30%. So at high concentration of oil in the emulsion layer, the introduction of magnet would increase the rate of floatation. However at low concentration, the magnetism effect would not be much different on the flotation rate.

Table 3.5 Effects of stirring and magnet on the kinetic parameters of oil floatation at 95^{o}C

Treatment	***k***	***N***
Manual stirring without magnet	0.0126	0.104
No stirring with magnet	0.0152	0.084
Stirring with magnet	0.0176	0.059
No stirring no magnet	0.0148	0.064

3.5 Concluding remarks

The discovery of the effect of HCl, heat and magnetic stirring in this study is very promising and need to be pursued to build up more information in the separation and recovery of oil from emulsion of different characteristics. In order to apply the results of this study to the pretreatment of POME in the recovery of the emulsified oil, further tests with the same procedure have to be carried out by using samples made up of lower crude palm oil-water mixture and crude palm oil-water-solid mixture that resembles POME more closely. Overall the result of our research could be summarized as follows:

- At a similar temperature, refined palm oil has a higher rate of flotation than the palm oil possibly due to the less viscosity, lower molecular weight and density and less content of phospholipids, β Carotene and free fatty acids.

- Adding HCl to either refined palm oil or palm oil can increase the flotation rates drastically. The modeling of the experimental data in Tables 3.1 and 3.2 showed that at 95^{o}C, adding HCl to refined palm oil and palm oil increased the k (kinetic rate constant) values by about 150% and 30% respectively. The better performance in refined palm oil could attribute to the difference in chemical content.

- Magnetic stirrer resulted in higher floatation rates (larger k values) than manual stirrer. This could be due to the more even mixing by magnetic stirrer than manual stirrer. Also, the magnetism effect increased the dependent of kinetic on the oil floatation at high concentration. Therefore, at high concentration the introduction of magnet would produce higher rate than that of without magnet even in the absence of stirring.

More tests, especially on a lower range of HCl concentrations, temperatures and ratios of oil-water mixture, need to be carried out for a clearer understanding of the oil separation behavior under those treatment conditions. More quantitative comparisons need to be done between treatments under different conditions to give a more precise understanding of the oil separation behavior.

Chapter 4

Rate of Solid Settlement in Sludge-Palm Oil Mixture

4.1 Introduction

In Chapter 3, the separation behavior of one of the three components of POME, oil from the oil in water mixture under the treatment conditions of HCl addition, heat and magnetic stirring has been studied and discussed. It was assumed that the other component, 5-7% solid had been completely removed either mechanically or chemically. However, the separation characteristics of the three components whether oil, solid and water, from each other will be different when each of them is placed in different medium under the same treatment conditions. The knowledge obtained from the study in Chapter 3 will not be sufficient to a full understanding of the response of POME to the treatment of HCl and heat. In this Chapter, the separation characteristics of solid from sludge-palm oil mixture under the treatment of HCl and heat in terms of rate of solid settlement has been investigated.

It had been difficult to observe and measure the solid settling rate by just mixing solid of POME in palm oil for the study of this chapter. Therefore, the sludge from the three phase decanter which contains solid and water was used to create the sludge-palm oil emulsion. In this case, the dispersed phase was the small amount of water from the sludge and the continuous phase was the palm oil. The solid from the sludge that usually contained cellulose and phospholipids, and thickener such as the gum from the plant cells could be dispersed in the palm oil continuous phase or in between the two liquid phases and temporarily stabilize the emulsion.

As can see from Stokes Law, particle size shows a strong relationship with settling velocity. The settling velocity of a solid particle is related to the square of the diameter of the particle. It is diagnostic of particle density as well as to the viscosity and density

of the fluid. In addition, it is also sensitive to the shape (roundness and sphericity) of the solid particles. According to Stokes Law, settling rate is directly proportional to particle size and difference in density between particles and fluid. At the same time, it is inversely proportional to viscosity of the medium. With respect to density difference and viscosity of medium, a change in temperature would cause difference in the settling rate. Since the solid particles in POME appeared to be different in type, size and shape according to Ho and Tan (1983), different models may be considered to fit its settling characteristics other than Stokes law. Changes in temperature would also lead to the destabilization of emulsions by affecting the solid-solution equilibrium of a system and precipitation of various species that affect the interfacial potential (Ramachandran and Somasundaran 1986).

The study done by Pichot, Spyropoulos and Norton (2009); Pacek, Ding, and Utomo (2007) on the effect of pH on the physical properties of the silica particles in the emulsion system can be used to evaluate the effect of HCl on the rate of solid settlement in POME emulsion because silica is one of the solid components of POME as reported by Ho and Tan (1983).

Since the range of methods adopted by previous researchers for separation of solid as described in section 2.2.2 of Chapter 2 were not practical for various reasons, this study aims at investigating the rate of solid settlement from sludge-palm oil mixture under the treatment of HCl and heat to increase the pool of knowledge in terms of solid settling characteristics in the continuous phase of palm oil which has never been studied before. It will also give insight to the design of POME pre-treatment system in future.

4.2 Problem Formulation and Approach

The suspended solid which consist of palm oil-solid-water in POME is the major cause of the difficulties in POME treatment. It cannot be separated mechanically with the present separating technology and it is the cause of the delayed hydraulic retention time (HRT) in the existing pond treatment of POME.

Besides the stability caused by the oil component, the solids that function as a coating layer around the oil droplets also prevent the separation of oil as well as solid from the suspended solid emulsion of POME. The surfactant or emulsifier and gum that may be present in the solid plant cells are the possible stabilizer of the emulsion.

HCl and heat treatment could be the method to destabilize the emulsion; however, it is difficult to study such possibilities by using raw POME due to its dark color and the complexity of solid content. Similar steps to the study in Chapter 3 of using synthesized samples resembling the POME are engaged to mitigate the problem.

In this chapter, the synthesized palm oil-sludge mixtures of different ratios are treated with or without 1% HCl at different temperature range as described later in the methodology section. The assumption in the study of this chapter is to disregard the effect of the small amount of water in the sludge that make up the sludge-palm oil emulsion. The investigation only focuses on the settling behavior of the solid in the continuous phase of palm oil. This will give a clearer understanding of the settling characteristics of solid in palm oil under the treatment of HCl, heat and different sludge-palm oil ratios.

The volume of solid settlement at every minute interval from the sludge-palm oil mixture is measured to determine the rate of solid settlement from sludge-palm oil emulsion.

All settling velocity model were designed to determine the settling velocity of solid particles in sludge at different solid concentration. For correlating the settling velocity with the corresponding concentration, one obtains the initial settling velocities by changing the concentration of the sample. Concentration of solid particles in palm oil-sludge emulsion is directly proportional to the volume of the sludge. This contributing to the reasoning of experiment carried out at different ratio of crude palm oil to sludge. Rate of separation for effect of hydrochloric acid and treatment temperatures carried out were determine by establishing a settling curve on the change of the interface height

with time. The term interface denotes the boundary between the immiscible phases of sludge and oil after emulsion destabilized.

Further investigations are required to study the settling characteristics of solid in the continuous phase of water and in the combination phase of oil-water in the following chapter.

4.3 Materials and Experimental Methods

4.3.1 Materials

Crude Palm Oil

The same crude palm oil used in the experiments for this study as in Chapter 3. The samples for the tests were made up of a mixture of the crude palm oil with decanter solid in a ratio of 80:20, 70:30, 60:40, 50:50, 40:60, 30:70 and 20:80 (v/v%). It is used for the study because this is the same type of oil present in the POME.

Decanter Solid

This solid was collected from the outlet of a three phase decanter used to separate the residue oil and solid from the sludge of the clarification unit at BLD Palm Oil Mill.

Hydrochloric Acid (HCl)

Refer to Appendix B

Equipments and Apparatus

Refer to Appendix B

Measurement Methods for Rate of Solid Settlement

The rate of solid settlement was determined by reading off the decrease in volume of solid (ml) disengaged from the mixture to settle to the bottom of the graduated measuring cylinder at every 1 minute time interval (Al-Zuhair 2004). The duration of the separating process was determined by the leveling off point of the settling curve where no more volume change of solid can be observed physically. Five runs were

carried out for every same test to eliminate statistical error and an average of the five sets of data was used to establish the settling curve. The initial readings before the leveling off point of the settling curve were used for establishing the kinetic model. Errors might arise in this experimental method due to the inconsistencies during the separation process. Some fine solids might be trapped in the oil but not observed physically. Higher temperature might cause convection current that make observation of leveling line difficult. An estimate had to be made in such cases.

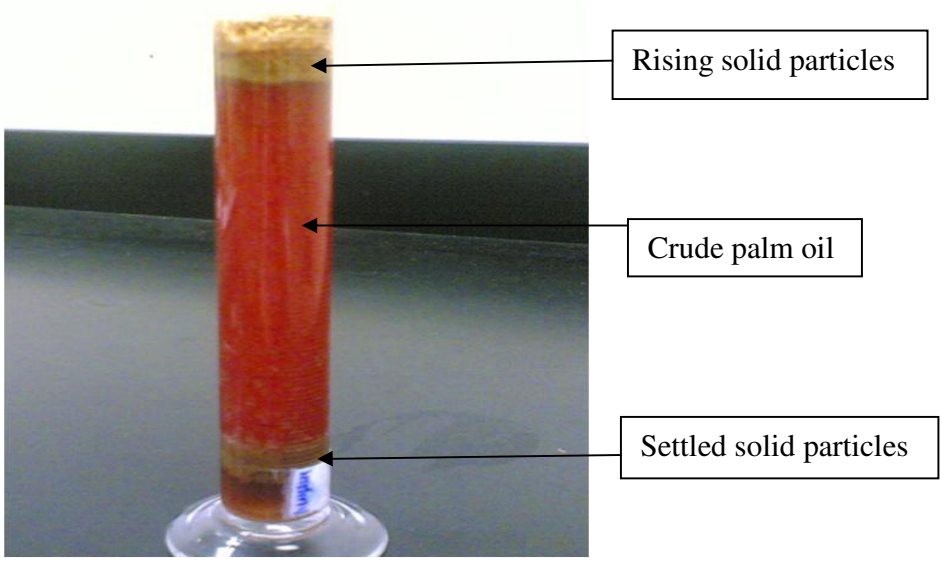
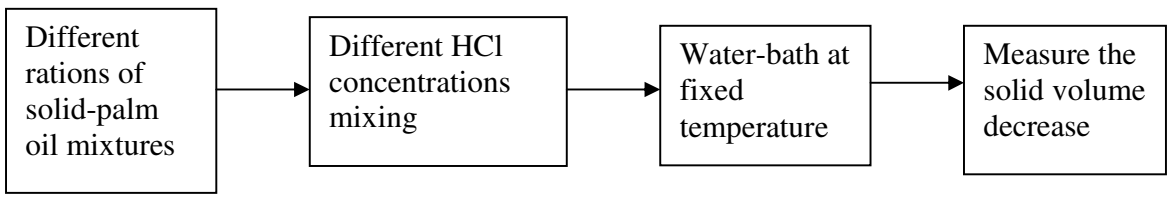


Figure 4.1: Measurement of solid settlement rate

General Experimental Procedure

The flow charts below show a general experimental procedure as described in Section 4.3.2a and 4.3.2b

For investigation of HCl effect



For investigation of heating effect

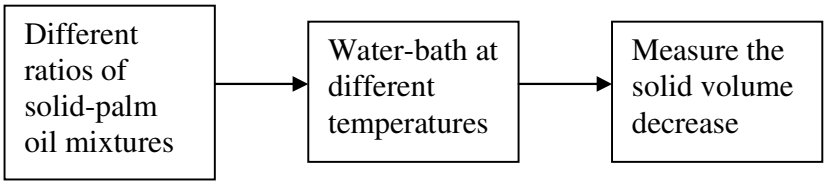


Figure 4.2 Flow chart of general experimental procedure

4.3.2a Treatment with HCl

Experiments were carried out with samples made up of a mixture of crude palm oil with solid at different ratio of 80:20, 70:30, 60:40, 50:50, 40:60, 30:70 and 20:80. The mixture of crude palm oil and solid was added with a 10ml of the prepared 10% (v/v) hydrochloric acid in a 500ml beaker to make the total mixture contain 1% of HCl. The mixture was warmed up to the temperature of approximately 65ºC in a water bath. Then, it was homogenized with a mixer for about 1 minute. Immediately after the mixing, the mixture was poured into a 100ml measuring cylinder. The measuring cylinder was submerged into the water bath set at fixed temperature range of 75-80ºC or 80-85ºC or 85-90ºC.

The changes of the interfacial height with time were recorded every minute. Experiments were repeated for five runs with the samples treated with HCl and without HCl to observe the effect of HCl on palm oil-solid separation.

4.3.2b Treatment with Heat

Experiments with the above procedures, but without addition of HCl were also repeated with the water bath temperature range of 80-85ºC and 85-90ºC to observe the effect of different temperatures on solid settling rate.

4.4 Results and Discussion

4.4.1 Treatment with HCl

The results in Figures 4.3 to 4.5 show that instead of increasing the solid settling rate of solid in palm oil medium, treatment with HCl at all tested temperature ranges slows it down. This seems to be in agreement with the literature review in 2.3.5 of chapter 2. The possible reason could be the neutralization of charge of solid particles such as silica by the cation of HCl that leads to a closely packed layer of silica particles between the oil-water interfaces which enhance the stability of the emulsion against coalescence (Horozov, Binks and Angew 2006; Vignati, Piazza and Lockhart 2003; Vermant et al. 2008). Another possible reason is the establishment of an electrostatic repulsion force between the ionic HCl and ionic bio-surfactant. More fundamental studies on the chemistry of the relationship between oil, solid and HCl is required for a better understanding of this phenomenon.

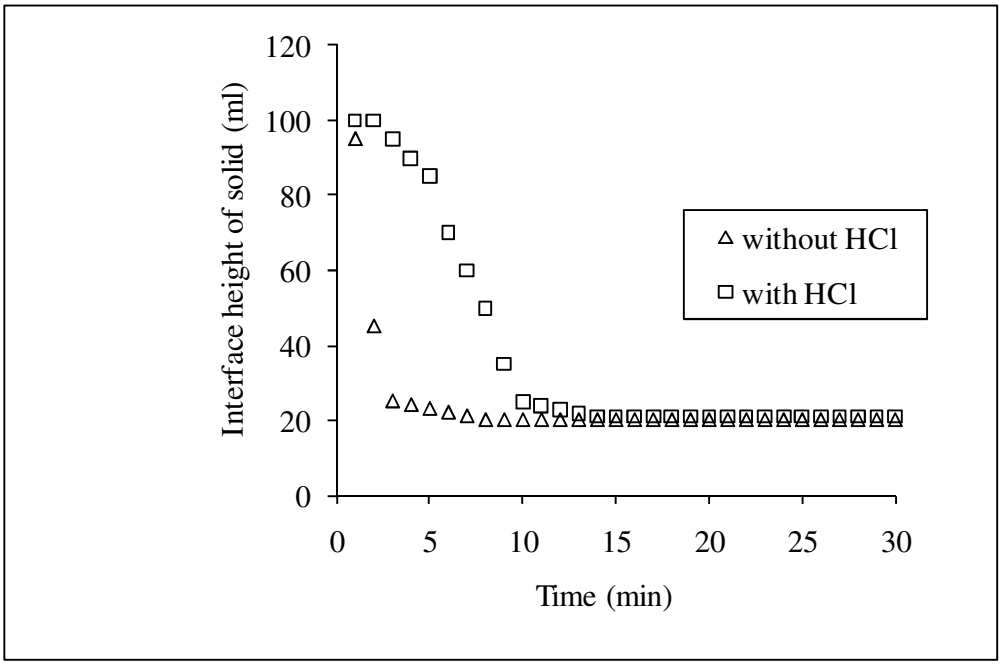


Figure 4.3: Effect of 1% HCl on the rate of solid settling of Palm oil-Solid mixture at 80:20 ratios at 80:20 ratios at 85-90ºC in 100ml sample.

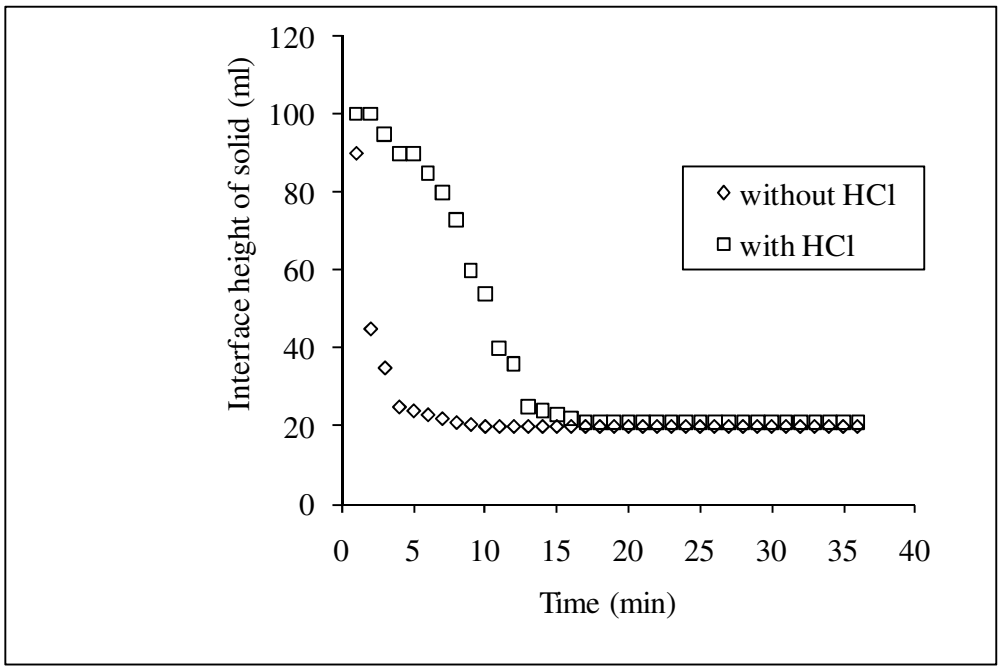


Figure 4.4: Effect of 1 % HCl on the rate of solid settling of Palm oil-Solid mixture at 80:20 ratios at 80:20 ratios at 80-85ºC in 100ml sample.

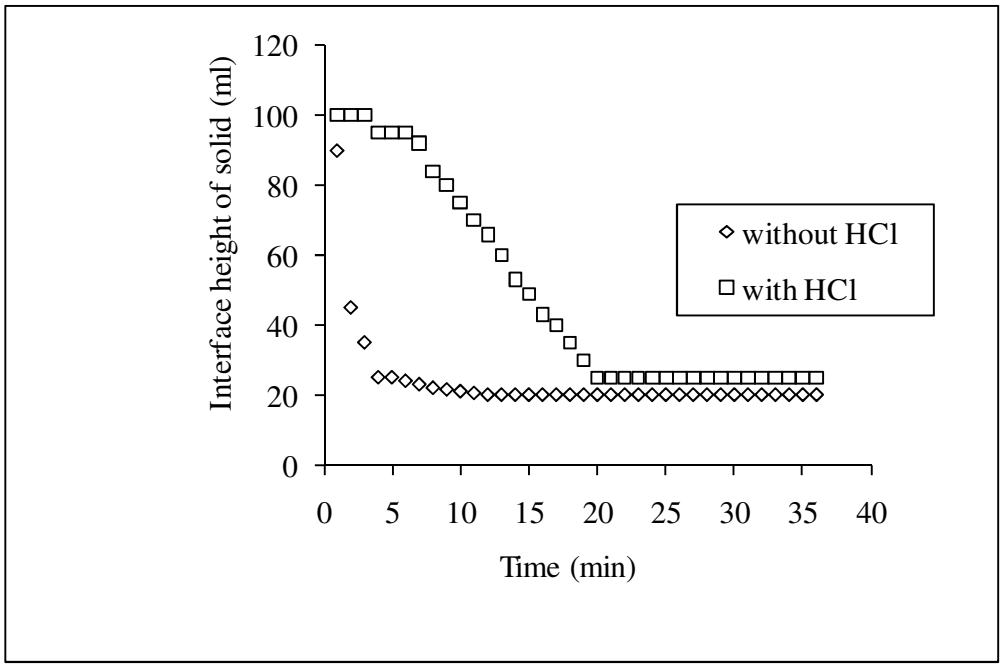


Figure 4.5: Effect of 1% HCl on the rate of solid settling of Palm oil-Solid mixture at 80:20 ratios at 80:20 ratios at 75-80ºC in 100ml

4.4.2 Treatment with Heat

A comparison between Figure 4.6 and Figure 4.7 shows that solid settling rate in Palm oil-Solid mixture of ratio 80:20 treated with 1% HCl increases significantly as temperature increases but the settling rate is much slower than the same mixture without 1% HCl at any temperature even the lowest 75-80^{0}C. Treatment with a temperature of 75-80^{0}C is sufficient to produce a faster solid settling rate in mixture without HCl treatment than treatment with 90^{0}C in mixtures treated with 1% HCl.

Figure 4.6 shows that the rate of solid settling in the palm oil-solid mixture without treatment of HCl does not increase with temperature as significantly as the same mixture treated with 1 % HCl. When temperature reaches above 90^{0}C in mixtures without treatment of 1% HCl, there appears to have a reverse effect. Some solid particles tend to rise together with the gas bubbles most probably generated by a convectional current of energized dissolved gas particles (Zieminski 1971). This is often a common phenomenon in the oil clarifier in the palm oil mills where the maximum operation temperature is usually 90^{0}C. The addition of HCl seemed to inhibit this reverse effect and lead to clearer solid settling effect. It will be a challenge in finding a compromise between enhancing the rate of solid settlement and rate of oil flotation because the later performs better at temperatures above 90^{0}C as discovered in chapter 3. Since addition of HCl can inhibit reverse effect of solid settling rate at above 90^{0}C to enhance clearer settling effect and enhance higher oil flotation rate as studied in chapter 3, should this approach be considered in POME treatment with respect to separation of oil and solid from its emulsion?

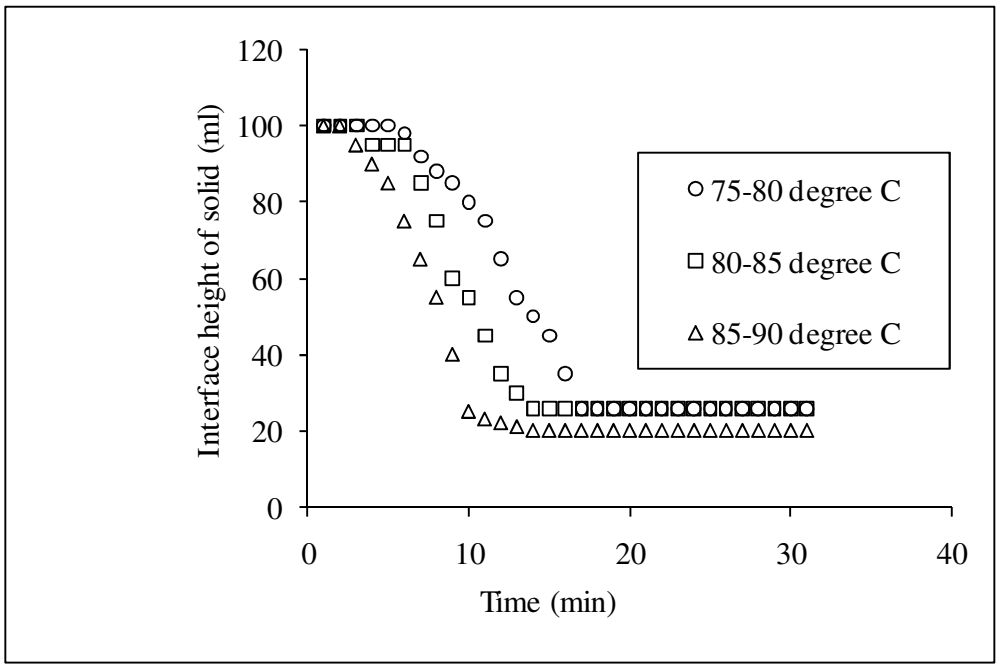


Figure 4.6: Effects of different temperatures on the solid Settling rate of Palm oil-Solid Ratio 80:20 with 1% HCl in 100ml sample.

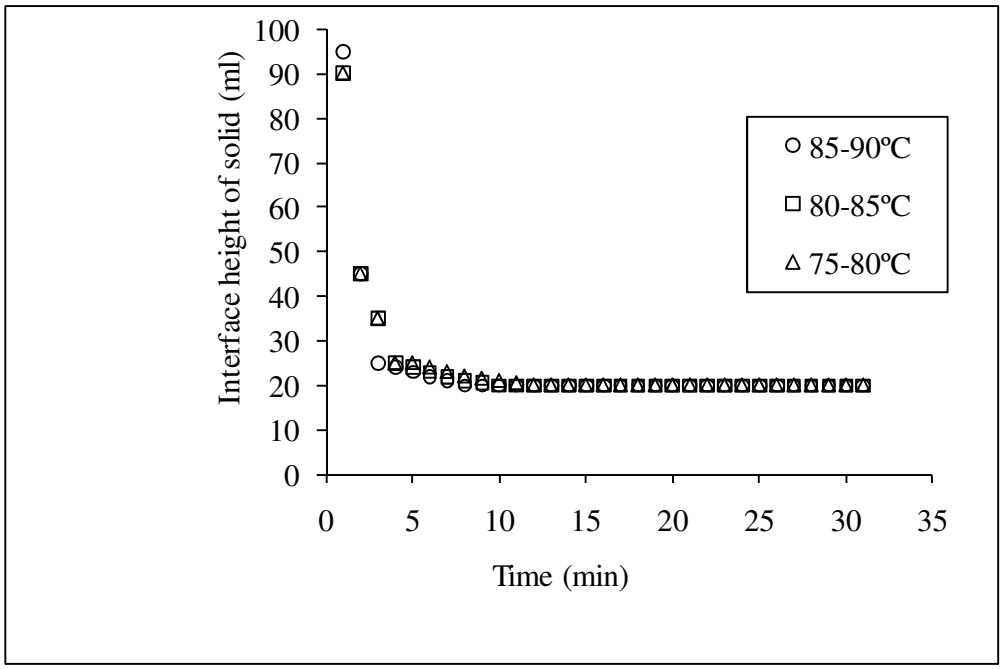


Figure 4.7: Effects of different temperatures on the solid Settling rate of Palm oil-Solid Ratio 80:20 without 1% HCl in 100ml sample.

The experimental result proved that temperature has significant effect on the separation of Palm oil-solid mixture and sediment of solid to the bottom regardless with or without the addition of hydrochloric acid. The slope of the settling curve indicates the settling rate of the solid. The bigger the slope of the settling curves regardless the positive or negative sign, the faster is the settling rate. Table 4.1 below shows the settling rate at 1 and 6 minute of the treatment with and without HCl at palm oil-solid ratio of 80:20. The slope of the settling curve is biggest at the temperature in the range of 85-90ºC, followed by 80-85ºC and 75-80ºC. The settling rate of solid increases fairly as the temperature of the water bath increases from 75-80ºC to 80-85ºC. As the temperature elevated to 85-90ºC, it appears to have the greatest effect on the sedimentation of solid for palm oil-solid emulsion. This agrees with stokes law (2.2) described later in section 4.5, because increase in temperature decreases the viscosity of oil (Dunchan 2000) and lead to a greater difference between the density of oil and solid phases.

Table 4.1 Settling Rate of System with Oil-Sludge Ratio 80:20

Temperature (ºC)	Settling Rate at 1min (mL/min)		Settling Rate at 6 min (mL/min)	
	with HCl	w/o HCl	with HCl	w/o HCl
75-80	-0.40	-25.29	-4.50	-0.70
80-85	-0.60	-25.29	-7.00	-0.80
85-90	-0.80	-30.14	-11.00	-1.10

4.4.3 Treatment with Dilution

As shown in Figures 4.8 and 4.9 higher palm oil-solid ratio also increases the rate of solid settling whether treated with or without 1% HCl at constant temperature. The increase in higher rate of solid settling in higher palm oil-solid ratio could be explained by the density difference between solid and oil phase according to stokes law. Also higher amount of solid will form a coating layer around oil droplets and the stabilizing agents present in the solid will stabilize the emulsion. As explained earlier, settling behavior of individual particles becomes different when the concentration of solids is high and the particles are so close to one another that they come into contact and interact

with one another easily. However, treatment with water dilution is not permitted by the Department of Environment in Malaysia. The method is therefore only feasible for study purposes.

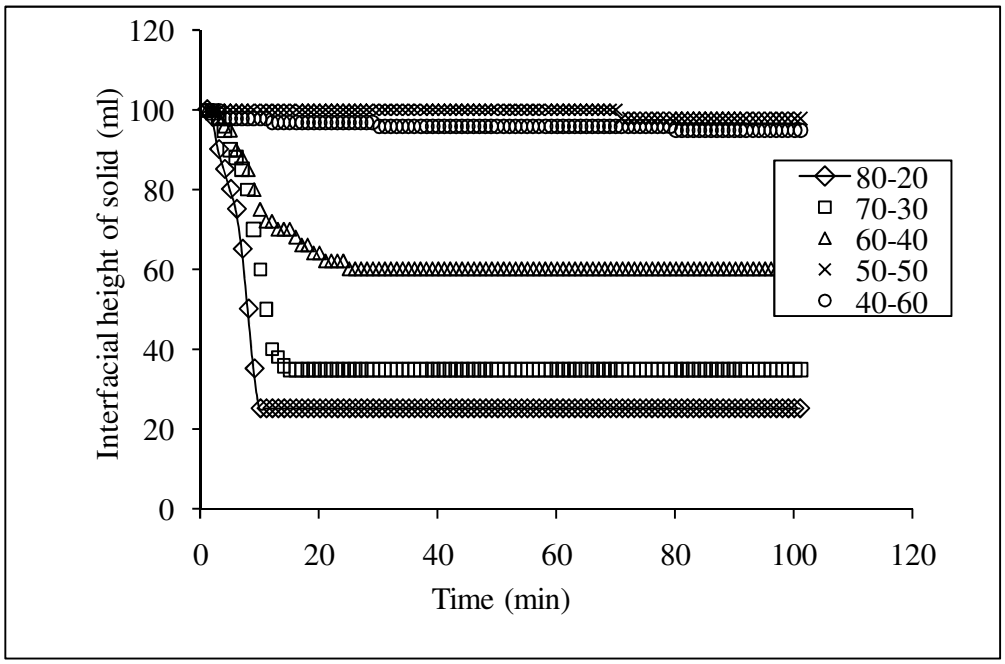


Figure 4.8: Effect of different Palm oil-solid Ratio on Solid Settling at temperature 85-90ºC with 1 % HCl in 100ml sample.

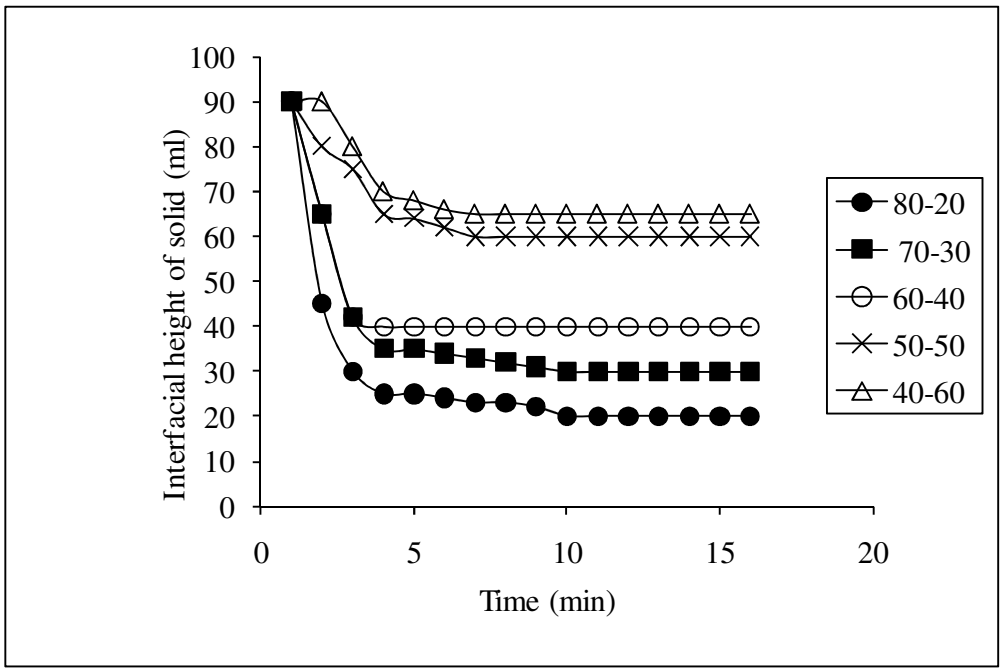


Figure 4.9: Effect of different Palm oil-solid Ratio on Solid Settling at Temperature 85-90ºC without 1 % HCl in 100ml sample

4.5 Data Analysis for Rate of Solid settlement in Solid-Palm oil Mixture

Emulsion breaking or de-emulsification, in this section of study attempted by treatment with HCl, heat and dilution, should be the initial step to enhance the settling of the solids in any emulsion. The emulsion breakdown mechanism results in oil coalesce and solid settling. All these are dependent on the phase volume, droplet size and physical environment of the system. It can be best represented by the Stokes equation (Richardson and Harker 2003):

$$V_s = \frac{2r^2}{9}\frac{g(\rho_p - \rho_f)}{\eta} \qquad (4.1)$$

Where V_s is the particle settling velocity, g is the acceleration of gravity, ρ_p is the density of the particles, ρ_f is the density of the fluid, η is the dynamic viscosity of the fluid and r is the radius of the particles. As can be seen from Stokes Law of (4.1), the difference in density between particles and fluid and the viscosity of the medium are strongly related to the settling velocity of the solid particles. Previous research on the improvement of the separation and settling of solids in oil-water-solid emulsion has been done using

different methods such as heating, adjustment of pH, treatment with chemicals, and even application of magnetic field.

By referring to (Font 1988); Coe and Clevenger (1916); Kynch (1952) introduced the solid flux concept for settler calculation, although various theoretical models and empirical models for the settling velocity were suggested. In general, two empirical models have been utilized practically for settler design with the solid flux theory. These are power model and exponential model which are defined as:

Power model:

$$V = kx^{-n} \tag{4.2}$$

Exponential model:

$$V = ke^{(-nx)} \tag{4.3}$$

The power model was utilized by Yoshioka at al. (1957), and Dick and Young (1972). The exponential model was used by Thomas (1963); Vesilind (1968); Smollen and Ekama (1984), etc. Cho et al. (1993) developed new models by starting with formula which is accepted universally for a flow-through porous media is that of Carman-Kozeny:

$$u_0 = \frac{\varepsilon^3}{(1-\varepsilon)^2}\frac{\Delta\rho}{K\eta a^2 L} \tag{4.4}$$

The average vertical velocity in the porous bed becomes as follows (Bird et al. (1960) and McCabe and Smith (1980) used the relation $u=u_o/\varepsilon$]:

$$u = \frac{u_0}{\varepsilon} = \frac{\varepsilon^2}{(1-\varepsilon)^2}\frac{\Delta\rho}{K\eta a^2 L} \tag{4.5}$$

In a column there is a movement of particles going down with a speed v with respect to the wall, and another up-flow liquid movement with a speed w with respect to the wall. The summation of the two speeds gives the settling velocity u.

$$u = v + w \tag{4.6}$$

The volumetric solid flux (1- ε) v is equal to the volumetric liquid flux EW, because the down flow solids displace the same volume of liquid. By putting this in settling velocity u (4.6), we get the down flow velocity of particles with respect to the wall:

$$V = \varepsilon u = u_0$$

$$V = \frac{\varepsilon^3}{(1-\varepsilon)^2} \frac{\Delta\rho}{K\eta a^2 L} \tag{4.7}$$

Physically the phenomena of hindered settling of flocculent particles like sludge can be assimilated to a filtration under the pressure equal to the apparent weight of the solid phase:

The apparent weight = gravity force – buoyancy

$$\Delta\rho / L = \beta(\rho_s - \rho_a) g \tag{4.8}$$

The slurry density is represented as:

$$\rho_a = \rho_s \beta + \rho(1-\beta) \tag{4.9}$$

Therefore we obtain $(\rho_s - \rho_a) = (1-\beta)(\rho_s - \rho_1)$ and relation (4.9) becomes:

$$\Delta\rho / L = \beta(1-\beta)(\rho_s - \rho_1) g \tag{4. 10}$$

Then the settling velocity of particles with respect to the wall can be represented as:

$$V = K' \frac{(1-\beta)^4}{\beta} e^{(-n'\beta)} \tag{4.11}$$

By using the density x instead of the volume fraction, (4.11) becomes:

$$V = k \frac{(1-n_1\chi)^4}{\chi} e^{(-n_2 x)} \tag{4.12}$$

If the volume fraction is negligible in comparison to 4.1, Cho et al. (1993) obtain a simpler form:

$$V = k \frac{e^{(-nx)}}{\chi} \tag{4.13}$$

On the other hand, if the viscosity term is constant, (4.12) becomes:

$$V = k \frac{(1-nx)^4}{x} \tag{4.14}$$

The representative models for settling velocity of solid which is chosen are equation (4.2), (4.3), (4.13) and (4.14). All equations have two parameters (Cho et al. 1993).

The results of the settling experiments with solid for four selected models are given in Table 4.2. Figure 4.10 and 4.11 below show the best fit obtained from various models. Because the models with three or more parameters are too complicated for practical application, these are not compared in this study.

Table 4.2 Kinetic Parameters of Different Models for Palm Oil Solid Settling Rate

Models	Temperature	With HCl			Without HCl		
		n	k	r^2	n	k	r^2
Power model $V=kX^{-n}$	75-80ºC	-1.0986	12.2681	0.9657	-1.0235	7.1299	0.9960
	80-85ºC	-1.2616	13.4691	0.9759	-1.0353	7.1306	0.9932
Yoshioka et al. (1957)	85-90ºC	-1.6232	17.5080	0.9768	-1.0001	6.8599	0.9940
Exponential model $V=ke^{-nX}$	75-80ºC	-2.9877	1.2560	0.9491	-2.7960	0.8487	0.9876
	80-85ºC	-3.4116	0.9909	0.9482	-2.8317	0.8271	0.9874
Vesilind (1968)	85-90ºC	-4.3244	0.6273	0.9212	-2.7205	0.8612	0.9773
New Model-1 $V=ke^{-nX}/X$	75-80ºC	-5.6958	0.1585	0.9694	-5.5041	0.1071	0.9821
	80-85ºC	-6.1196	0.1251	0.9655	-5.5398	0.1044	0.9827
Cho et al. (1993)	85-90ºC	-7.0325	0.0792	0.9464	-5.4285	0.1087	0.9773
New Model-2 $V=k(1-nX)^4/X$	75-80ºC	-3.0551	0.0384	0.9824	-2.7724	0.0472	0.9972
	80-85ºC	-3.5630	0.0459	0.9817	-2.8693	0.0519	0.9968
Cho et al. (1993)	85-90ºC	-4.8909	0.0490	0.9732	-3.1227	0.0688	0.9933

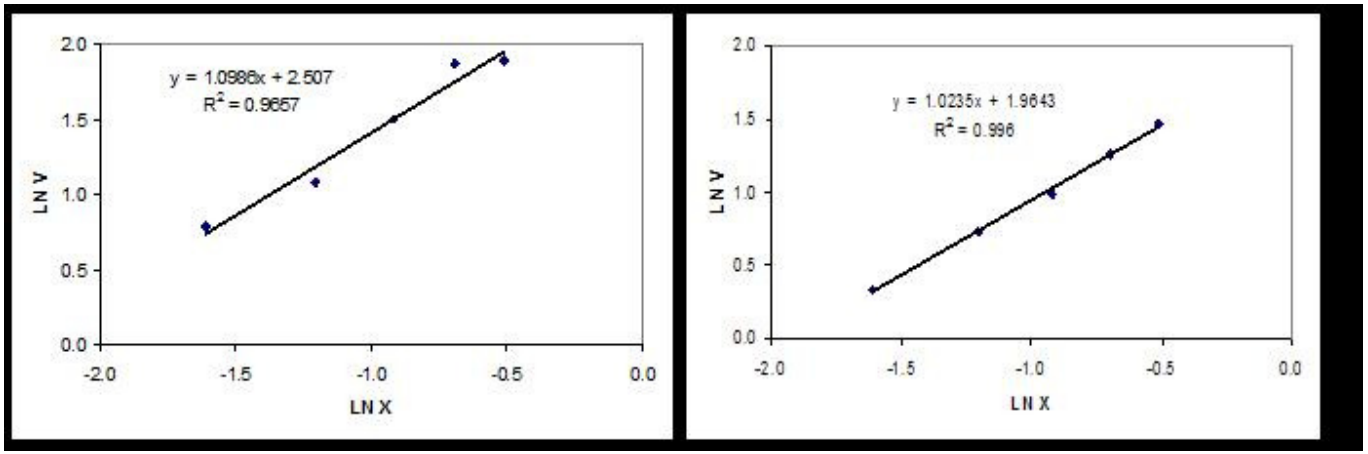


Figure 4.10 Correlation with Yoshioka power model $V=kX^{-n}$ (a) with HCl (b) w/o HCl

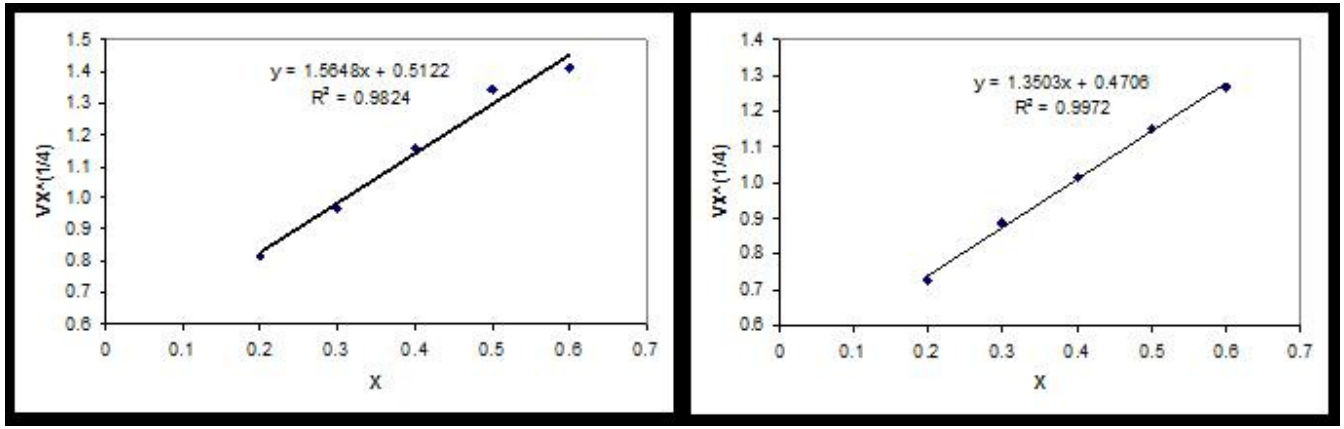


Figure 4.11: Correlation with Cho new developed power model $V=k(1-nX)^4/X$ (a) with HCl (b) without HCl.

After comparing the R^2 values of different models in Figure 4.10 and 4.11, the power model and the new developed model fitted well with the experimental data in this study. The latter was better than the former. The kinetic rate constant of solid settling in solid-palm oil mixture treated with HCl increases as temperature increases while the kinetic rate constant of solid settling in the sample without HCl treatment increases as temperature increases but decreases again at temperature near 90^0C. It appears as if the treatment with HCl helps in reducing the effect of convection current that cause the solid particles to rise upward at 90^0C though it slows down the settling rate. According to Flores, Ye and, Singh (2005), many other factors such as PH, ionic strength and the type of emulsifiers present can affect the heat stability of the emulsion. Monahan, McClements, and German (1996), Sliwinski et al. (2003) and Euston, Finnigan, and Hirst (2000) reported that certain emulsion breaking occurs at particular temperature range only. Higher temperature may not necessarily increase oil droplets aggregation because of inter-droplet and intra-droplet interaction which are favoured at different temperature range. The type and concentration of emulsifier or surfactant present will also determine the emulsion breaking response to heat treatment at different temperature range (Hunt and Dalgleish 1995; Josephine and Dalgleish 1995). However, the reasons for the treatment with HCl in reducing the effect of convection current that cause the solid particles to rise upward at 90^0C though it slows down the settling rate could be as follows: High temperature treatment could cause hydrolysis of surfactants such as egg phospholipids to become fatty acids. These acids create an acidic environment that will enhance the coalescence of oil droplets (Chansiri et al. 1999). HCl treatment could have promoted the coalescence of oil droplets by neutralizing the negative charges of the oil droplets that facilitate coalescence of oil droplets. This could have caused a clearer layer of oil floating on top of the mixture. However, HCl treatment which consequently leads to the lowering of PH could have neutralized the charges of solid particles that packed closely between the oil droplets which enhance the stability of the emulsion against coalescence (Vignati, Piazza, and Lockhart 2003; Horozov, Binks, and Angew 2006; Vermant et al. 2008). This could be the cause for the slower solid settlement rate.

4.6 Concluding remarks

This work has shown that the hydrochloric acid has not been very effective in improving the settling rates of solid. One of the major factors that influence the emulsion stability was the temperature because settling rates increased more significantly with the increase in temperature. However, at very high temperature, 90^0C, rising solid occurred and this could affect the efficiency of palm oil-solid separation. HCl helps in reducing the effect of convection current that cause the solid particles to rise upward at 90^0C though it slows down the settling rate. A higher palm oil-solid ratio also exhibited faster solid settling rates. This presented another difficulty in separating solid from POME because it contained very low percentage of oil. Further investigation into the separation characteristics of solid from solid-water mixture and solid-palm oil-water mixture may increase the pool of research knowledge in this particular occurrence in Malaysia which is part of this beautiful world.

Chapter 5

Rate of Solid Settlement In Decanter Solid-Water and Clarifier Sludge-water mixtures

5.1 Introduction

From the description of the title, it is obvious that this Chapter is a continuation of the investigation on the rate of solid settlement of Chapter 4, but with the use of two other types of mixtures that may resemble POME. With the discovery of the solid settlement characteristics in sludge-palm oil mixture of Chapter 4, further investigation on the solid settlement characteristics in the other medium such as water only and oil-water mixture was essential for a deeper understanding of the separation characteristics of the solid component of POME.

Decanter solid was the solid output of the three phase decanter that separated the oil, solid and liquid sludge of the settled sludge of the clarifier. Its content was similar to the solid present in POME. Clarifier sludge was the settled underflow of the clarifier. It contained oil, water and solid in a proportion described in section 5.3.1. Clarifier sludge was also used for this study as it was the closest resemblance of POME though the proportion of oil, water and solid were different.

Since clarifier sludge was closer to POME, it had similar emulsion characteristics as POME too. The interaction mechanisms of the three components present should be close to the description of the POME emulsion in Section 2.3 of Chapter 2. Addition of water to the clarifier sludge would alter the solid-liquid equilibrium point and treatment with heat and HCl (change of PH) would cause changes in the physical properties of the

solid, oil and water in different ways described by various researchers (Pacek, Ding, and, Utomo 2007; Pichot, Spyropoulos, and Norton 2009; Ramachandran and Somasundaran 1986). These changes would lead to changes in the rate of solid settlement in the mixture

Decanter solid-water mixture however was more like a suspension because there was very little water and oil content as shown in Section 5.3.1. Stokes law was still applicable for the investigation of the solid settling behavior as the way it was for sludge-palm oil mixtures of Chapter 4. Therefore, a positive impact on the rate of solid settlement would be expected with treatment of heat and dilution. However, treatment with HCl would be a new attempt.

Destabilization of centrifuge wastewater or POME is best illustrated by sedimentation, also known as settling. The rate of solid settlement as well as rate of oil flotation is the best indication of treatment efficiency of the wastewater in concern. It can be used to decide if the treatment method is feasible. This study will definitely increase the knowledge on the emulsion characteristics of POME which had not been studied by other researchers before.

Therefore the objectives of this chapter are again the study of the rate of solid settlement under the treatment conditions of HCl, heat and dilution, but using two other synthesized mixtures that resemble POME. They are the Decanter solid – water and Clarifier sludge-water mixtures.

5.2 Problem Formulation and Approach

The suspended solid emulsion which consist of palm oil-solid-water in POME cannot be demulsified mechanically with the present separating technology and it is the cause of the delayed hydraulic retention time (HRT) in the existing pond treatment of POME.
After gaining some comprehension of the separation characteristics of oil from the continuous phase of water and solid from the continuous phase of palm oil, The

separation characteristics of solid from the continuous phase of a): water only and b): oil-water mixture must also be understood.

a) Water (93-95%) is the largest of the three components of POME. It is different from palm oil in viscosity, density, specific heat capacity and also chemical composition. Therefore, decanter solid-water mixture was used as the first part of the study of this chapter.
b) It is difficult to use the raw POME for investigation of the separation characteristics of each component because of the high concentration of solid, very low concentration of oil and the dark coloration. Therefore, a study on the separation behavior of solid from solid-palm oil-water (Clarifier sludge-water) mixtures, which is the closest resemblance of POME, would provide a closer understanding of the solid settling characteristics in POME.

As a continued study of Chapter 3 and 4, the Decanter solid-water mixtures and Solid-palm oil-water (clarifier sludge-water) mixtures of different ratios specified in the methodology section were treated with 0%, 0/5% and 1% HCl and heating temperatures of 70^0C, 80^0C and 90^0C.

The rate of solid settlement from each sample was determined by reading off the decrease in volume of solid in the solid-water mixtures and clarifier sludge-water mixtures at every minute interval. The same test was run four times to eliminate errors that might be caused experimentally or inaccurate reading obtained due to inconsistent settling phenomena. The results are presented in graphs of settling curves with interfacial height of solid (ml) against time (minute) and the initial data are analyzed to establish the settling velocity model.

Further test with the real POME with same treatment have to be carried out with spectrophotometer or turbidimeter to determine the rate of solid settlement.

5.3 Materials and Experimental Methods

5.3.1 Materials

Decanter Solid

This solid was collected from the outlet of a three phase decanter used to separate the residue oil and solid from the sludge of the clarification unit at BLD Palm Oil Mill. It contains palm oil (%), solid (%) and water (%).

Clarifier sludge

The clarifier sludge was collected from the outlet of the clarifier tank of the clarification station of BLD Palm Oil Mill. It is a mixture of palm oil (10%), solid (10%) and water (80%). It was further diluted to designated concentrations to suit the experimental purposes.

Hydrochloric Acid (HCl)

Refer to Appendix B

Equipments and Apparatus

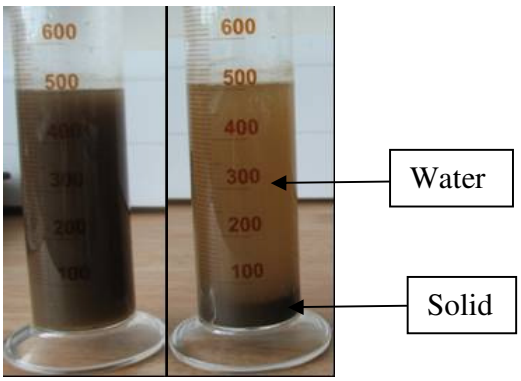
A 15 gallon water-bath with heat controller was used for the tests on the effect of different temperatures on the rate of solid settlement.

Figure 5.1: 15 gallons Hot water bath

500 ml graduated measuring cylinders were used as containers for the study of the rate of solid settlement in this chapter.

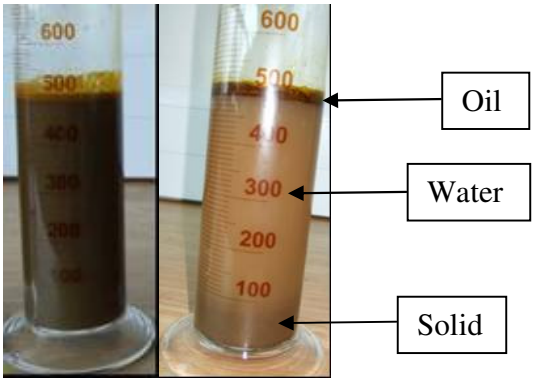
Measurement Methods for Rate of Solid settlement

The measurement method for the study in this chapter is similar to the method used in Chapter 4. Figure 5.1 and 5.2 showed the appearance of the different mixtures before and after solid settlement. The decrease in volume of solid can be read directly from the 500ml graduated measuring cylinders. The rate of solid settlement was determined by reading off the decrease in volume of solid (ml) disengaged from the mixture to settle to the bottom of the graduated measuring cylinder at every 1 minute time interval (Al-Zuhair, 2004). Readings were taken until no more volume change of solid can be observed physically. Four runs instead of five were carried out for every same test because of inconvenience in obtaining and keeping large amount of raw materials for the tests. The average of the four sets of data was used to establish the settling curve. The initial readings before the leveling off point of the settling curve were used for establishing the settling rate model. Reading errors might arise due to the inconsistent separation process caused by convection current and very fine solids being trapped in the water beyond the observation capability of naked eye. Estimation had to be made in such cases.



Before After

Figure 5.2: Measurement of solid separation process in decanter solid-water mixture



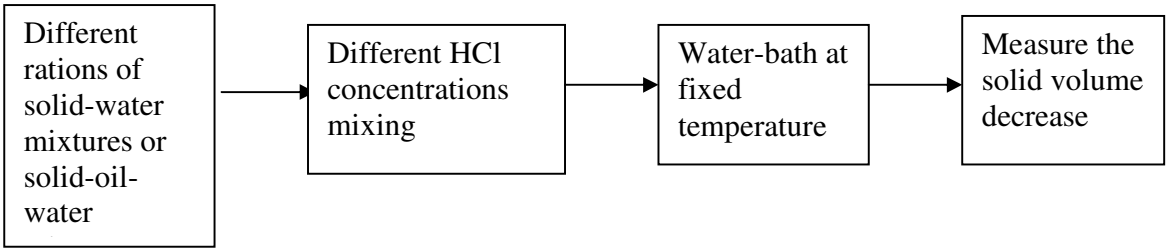
Before After

Figure 5.3: Measurement of solid separation process in solid-palm oil-water (Clarifier sludge-water) mixture

General Experimental Procedure

The flow charts below show a general experimental procedure as described in Section 5.3.2a and 5.3.2b

For investigation of HCl effect



For investigation of heating effect

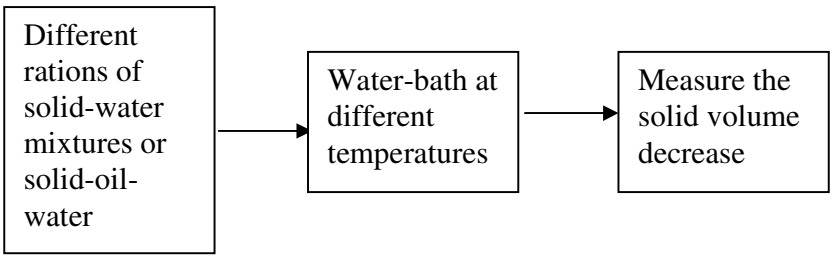


Figure 5.4: Flow chart of general experimental procedure

5.3.2a Treatment with HCl

Both Decanter solid-water mixture and solid-palm oil-water mixtures of different ratios were treated with HCl to investigate its effect on the rate of solid settlement.

Decanter solid-water mixtures

Four graduated glass cylinders filled with 500ml of desired ratio of decanter solid-water mixture (2% solid: 98% water, 5% solid: 95% water and 10% solid: 90% water) and 1% HCl were placed into a temperature controlled water-bath tank that filled with 15 gallons of water at 75^0C. The changes of the interfacial volume with time were recorded. Statistical analysis was performed on the collected data to determine the separation rate with HCl treatment. The procedure was repeated by treatment with 0.5% HCl on the samples of same ratios at 75^0C.

Solid-palm oil-water (Clarifier sludge-water) mixtures

Four graduated glass cylinders of 500ml were placed in a water-bath tank filled with 15 gallons of water with its temperature adjusted at 80^0C and 90^0C each respective time. The cylinders were then filled with preheated samples of clarifier sludge (palm oil-solid-water)-water mixture with the addition of 0.5% or 1% HCl to the samples to observe the effect of HCl on the separation performance. The changes of the interfacial height with time were recorded.

5.3.2b Treatment with Heat

Decanter solid-water mixtures

The above procedure used for treatment with HCl was repeated by heating the samples of same ratios without addition of HCl in the water-bath with temperature fixed at 70^0C or 80^0C or 90^0C.

The separation performance in temperature and HCl treatment could then be compared. The objective of performing these experiments was to examine the solid separation velocity when either heat or HCl is applied.

Solid-palm oil-water (Clarifier sludge-water) mixtures

Four more runs were carried out at 70^0C, 80^0C and 90^0C with the same procedure used for HCl treatment to observe the effect of Heat on the separation performance.

5.4 Results and Discussion

5.4.1 Treatment with HCl on Decanter solid-water mixtures

This study showed that treatment with HCl does not improve the solid settling rate in solid-water mixture as in palm oil-water mixture (Figure.5.5). But it does not slow the rate down as much as in solid-palm oil mixture in Chapter 4. The difference in phenomenon could be caused by the difference between the viscosity of oil and water. This led to a difference in density difference in the two phases of solid-palm oil or solid-water and resulted in different rate of solid settlement as described by Stokes law. Apart from that, treatment with HCl resulted in a clearer supernatant water layer. A better zone settling phenomenon as described by Kynch theory (Renko 1998; Kynch 1952) may have occurred with the treatment. Renko (1998) stated that if the solid concentration is high enough, there is significant interaction between the particles and in a batch settling test they start to settle together having a clear interface between the suspension and the supernatant liquid'. A decrease in PH could have neutralized the surface charges of the solid quite slowly resulting in a closely packed solid cluster (Vignati, Piazza, and Lockhart 2003; Horozov, Binks, and Angew 2006; Vermant et al. 2008) which settled together leaving a clearer supernatant. Increase in HCl concentration does not improve its effect. This phenomenon appears similar to the treatment of palm oil-water mixture with increased HCl concentration. More investigations is required to confirm if the concentration of solid in water will affect the performance of different HCl concentrations as in the case of palm oil-water mixture.

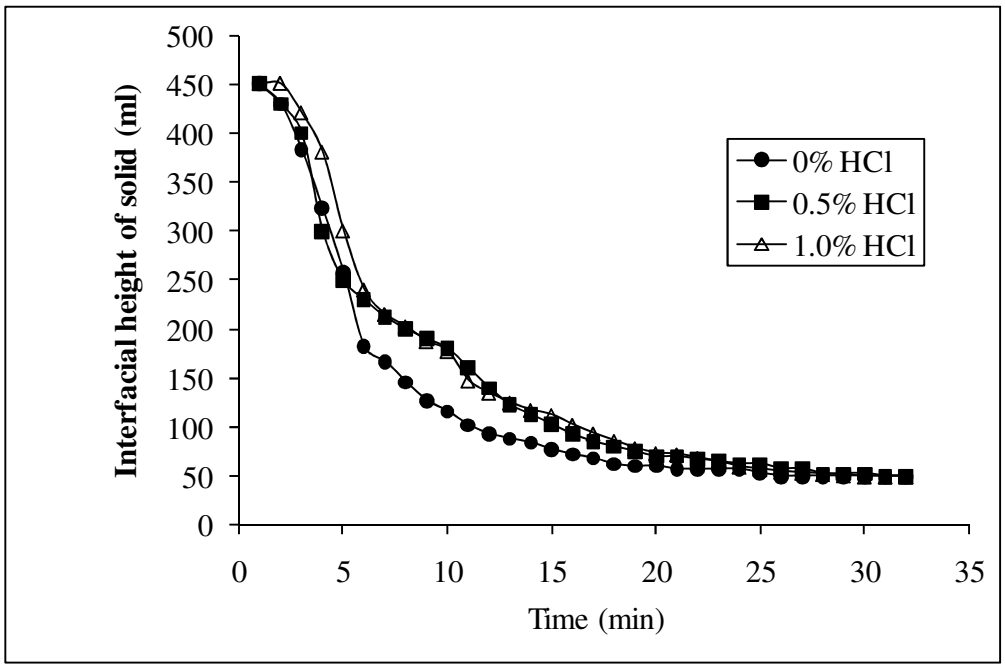


Figure 5.5 Solid Settling in Decanter solid-water mixture (2:98v/v) ratios treated with HCl of different concentrations at 75^0C in 500ml sample.

5.4.2 Treatment with HCl on Solid-palm oil-water (Clarifier sludge-water) mixtures.

Figure 5.6 shows that treatment with 0.5% of HCl increased the solid settling rate slightly and improved the clarity of the supernatant in palm oil-solid-water mixture that is clarifier underflow-water mixture as compared to treatment without HCl. This occurrence is the opposite of that of the previous two samples: solid-palm oil mixture and solid-water. The presence of oil and an increase in oil separation rate caused by HCl might have resulted in a speedier settling of suspended solids initially trapped with oil and water emulsion. However, an increase in HCl concentration did not improve its effect. Again, More investigations is required to confirm if the concentration ratio of the three components, solid, oil and water will affect the performance of different HCl concentrations as in the case of palm oil-water mixture. More should be done to produce data that may bring more discoveries in the separation characteristics of oil, solid and water in POME by treatment with HCl.

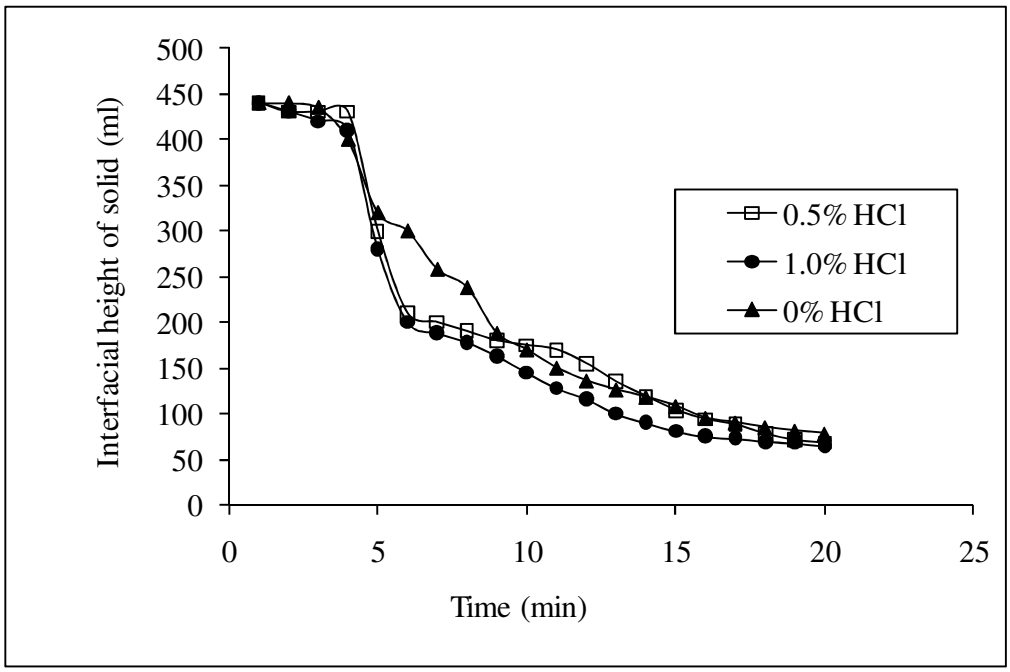


Figure 5.6 solid settling for Clarifier underflow-water mixture of (20:80v/v) ratio treated with different concentrations of HCl at 80^0C in 500ml sample.

5.4.3 Treatment with Heat on Decanter solid-water mixtures

Similar to the rate of oil flotation in palm oil-water mixture and rate of solid settlement in solid-palm oil mixture, treatment with different temperatures improved the solid settling rate in solid-water mixture (see Figure 5.7). But the effect was not as great as in the former two cases. Unlike the oil, the solid settling rate did not increase proportionally with increasing temperatures. It gave a reverse effect when the temperature reaches 90^0C which is similar to the occurrence in solid-palm oil mixture when it was treated with a temperature of 90^0C. This was due to the occurrence of a convectional current that brings the settling solid particles upward again with the gas bubbles which began to escape as steam (Zieminski 1971). Stokes principle of density difference caused by decrease in viscosity due to increasing temperature also applied to the solid settling rate in this case.

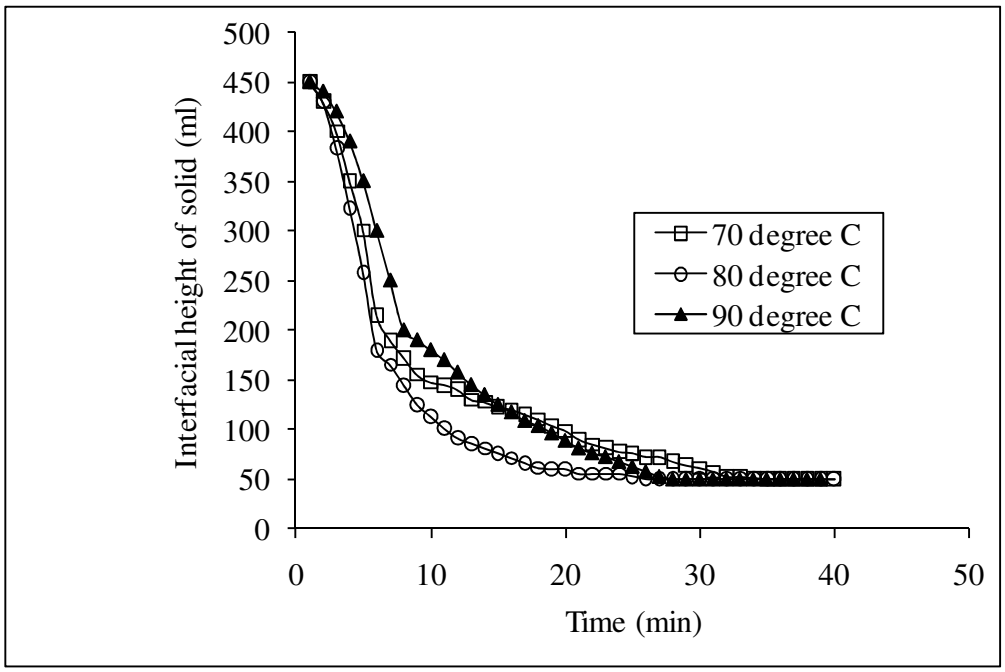


Figure 5.7 solid settling in Decanter solid-water mixture of (2:98 v/v) ratio with different temperatures in 500ml sample.

5.4.4 Treatment with Heat on Solid-palm oil-water mixtures (Clarifier sludge)

The result shown in Figure 5.8 expressed a minimal increase in rate of solid settlement with an increase in temperature on the clarifier sludge of 20:80 ratios (v/v). A temperature range of 80^0C to 90^0C appeared more suitable for solid settlement.

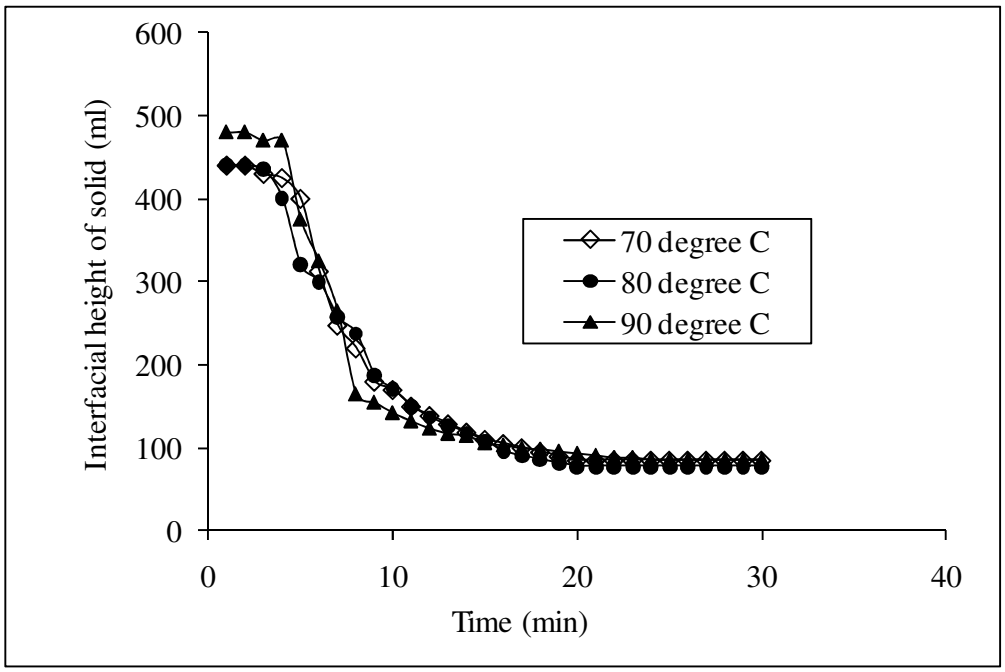


Figure 5.8 solid settling for Clarifier underflow-water mixture of (20:80 v/v) ratio treated with different temperatures.

5.4.5 Treatment with Dilution on Decanter solid-water mixtures

As explained by Stokes law, the higher dilution reduces the interaction between solid particles and increases the difference in densities of the two phases and thus speeds up the settling rate of individual solid particles. In Figure 5.9, higher dilution shows marked improvement in the solid settling rate in decanter solid-water mixture.

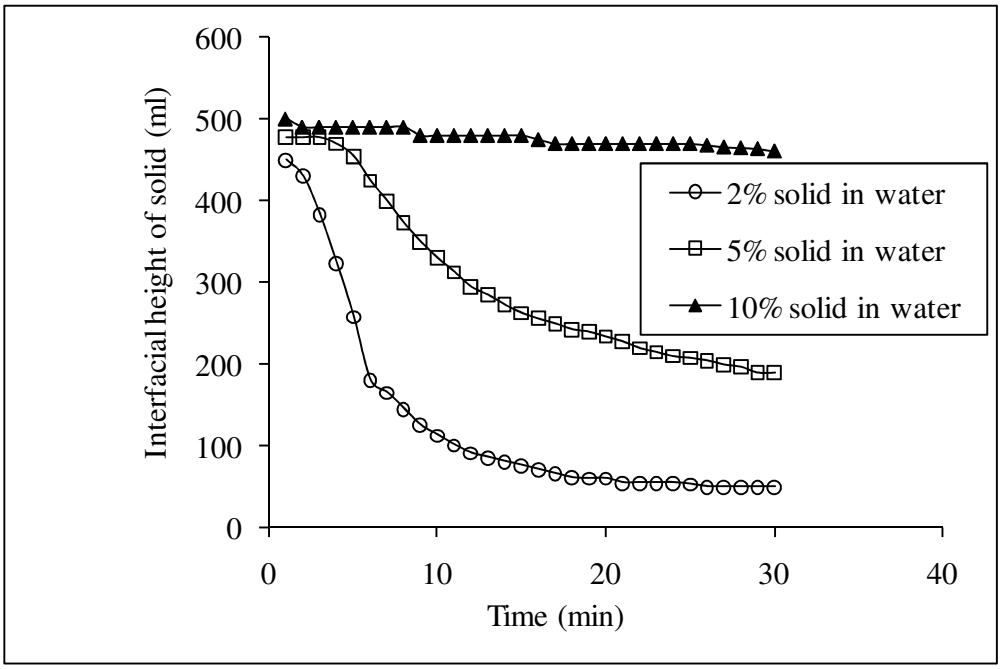


Figure 5.9 the solid settling rate in Decanter solid-water mixture of different dilutions treated with fixed temperature of 80^0C in 500ml sample

5.4.6 Treatment with Dilution on Solid-palm oil-water (Clarifier sludge-water) mixtures

In the clarifier underflow-water mixture (palm oil-solid-water mixture), the dilution seems to give most significant improvement in solid settling rate (Figure 5.10) though not as much as that of solid-water mixture due to the presence of oil. Treatment with HCl and temperature give slight improvement (Figure 5.6, 5.8). However, treatment with water dilution is not permitted by the Department of Environment in Malaysia. The method is therefore only feasible for study purpose. Since clarifier underflow-water mixture (palm oil-solid-water mixture) is the closest representation of the actual POME, the experimental results therefore are not very supportive in POME pre-treatment with HCl and elevated temperature.

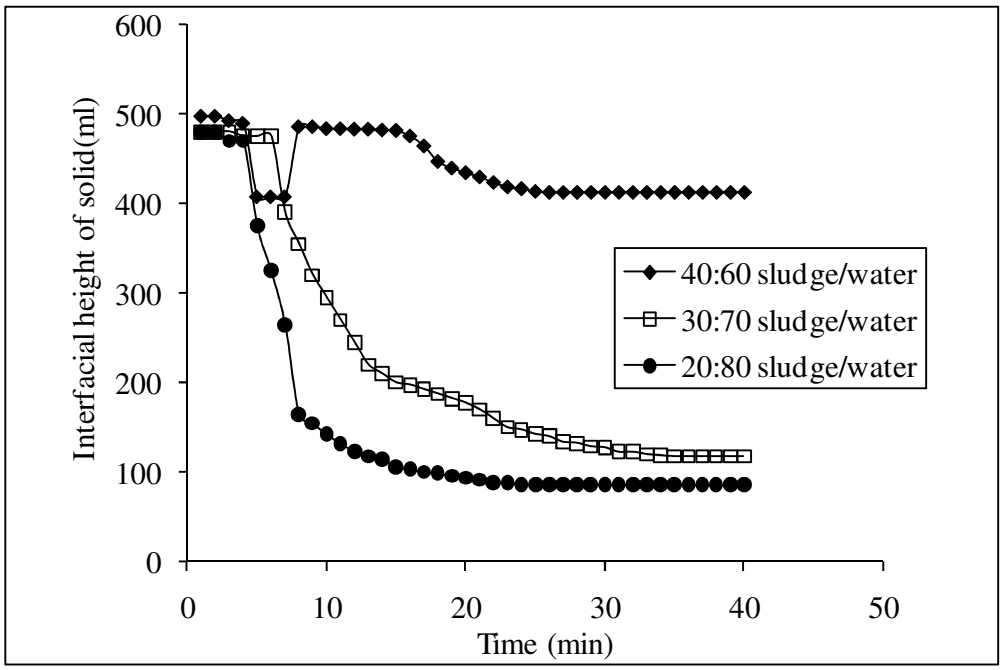


Figure 5.10 solid settling for different Ratios of clarifier underflow- water mixtures at a fixed temperature of 90^0C

5.5 Data Analysis for Rate of Solid settlement in Solid-water and Clarifier Underflow-water Mixtures

The solid settling velocity depends on the area of the cylinder, solid settling volume and time taken for the solid to settle in decanter solid-water mixture and clarifier sludge-water emulsion. The rate of change of volume *dV/dt* is obtained experimentally.

$$\frac{dV}{dt} = A_c \frac{dh}{dt} = A_c V_s \tag{5.1}$$

To determine V_s, the following expression is used:

$$V_s = \frac{1}{A_c} \frac{dV}{dt} \tag{5.2}$$

Where, A_c is the area of cylinder (cm^2), which can be calculated by using equation

$$A_c = \frac{\pi D^2}{4} \tag{5.3}$$

Where, D is the diameter of the cylinder.

(Anna 1998)

The rate of change of velocity shown in Figure 5.11, 5.12 and 5.13 below illustrate the trends of solid settling rate for different concentrations of decanter solid-water mixture (2% decanter solid : 98% water, 5% decanter solid : 95% water and 10% decanter solid : 90% water) as shown in Figure 5.9. It is obvious that the smaller concentration of decanter solid (2% decanter solid: 98% water) takes shorter time to settle and larger decanter solid concentration requires longer time to completely settle. This is because there is less amount of solid that needs to be separated and less inter-particle interaction in 2% decanter solid: 98% water mixture. The greater difference in densities between the two phases is another reason for the faster settling rate. Figure 5.11 clearly shows a temperature of 80ºC seems to have the best effect on solid settling rate where it settles quicker and smoother. Unlike oil-water emulsion separation, elevated temperature (90ºC) does not seem to have positive effect on solid settling rate but instead, it gives a convectional (reverse) effect, in which the particles collision between the solid particles in the mixture slowed down the settling velocity and the suspended solids float upward. Figure 5.12 and 5.13 shows slower solid settling rate in all temperatures because of the higher concentration of solid content.

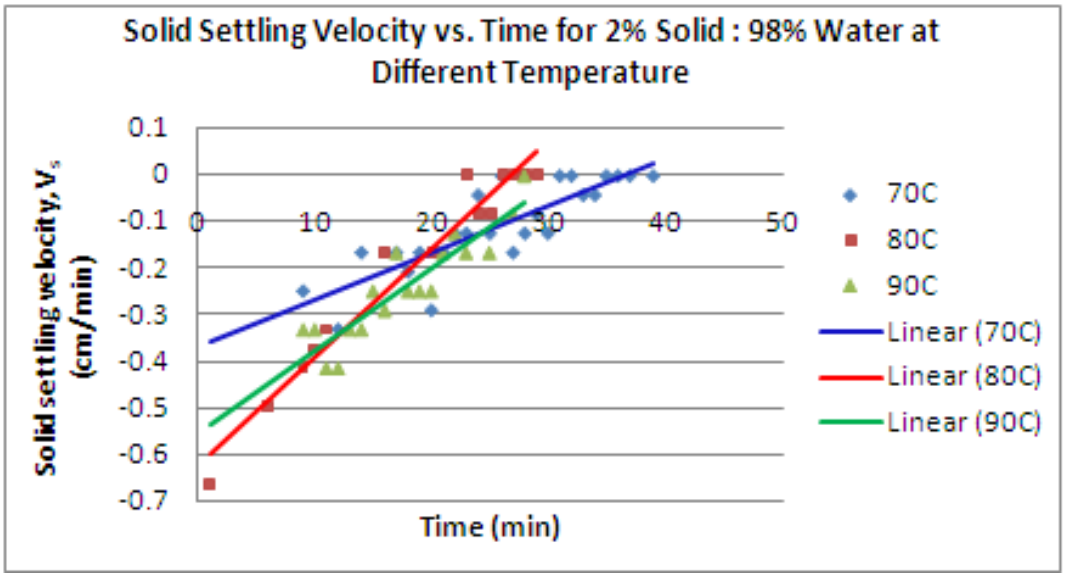


Figure 5.11 Solid settling velocities (cm/min) with time (min) in decanter solid-water mixtures using heat treatment.

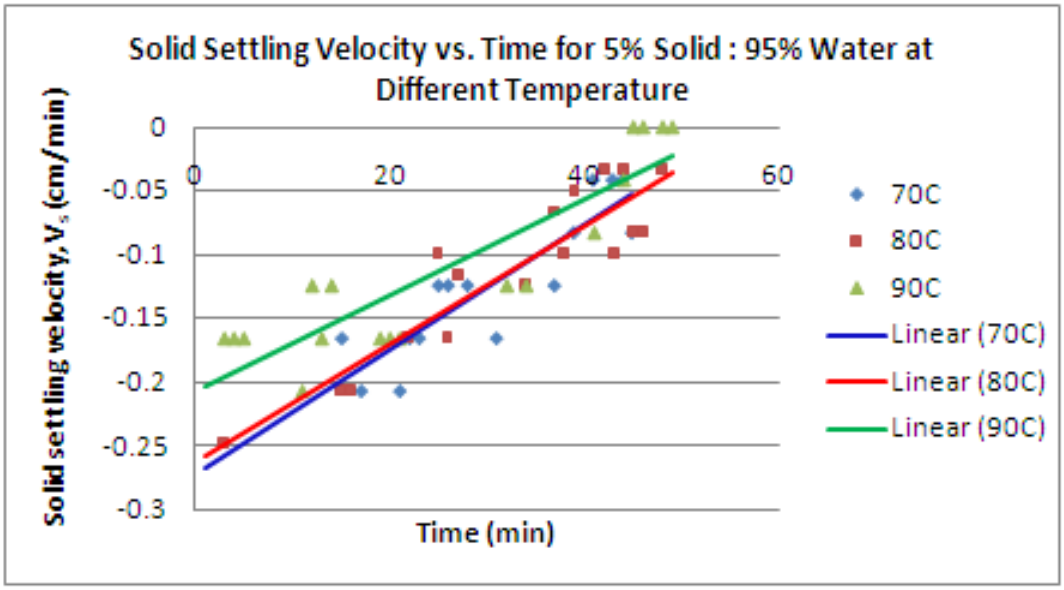


Figure 5.12 Solid settling velocities (cm/min) with time (min) in decanter solid-water mixtures using heat treatment

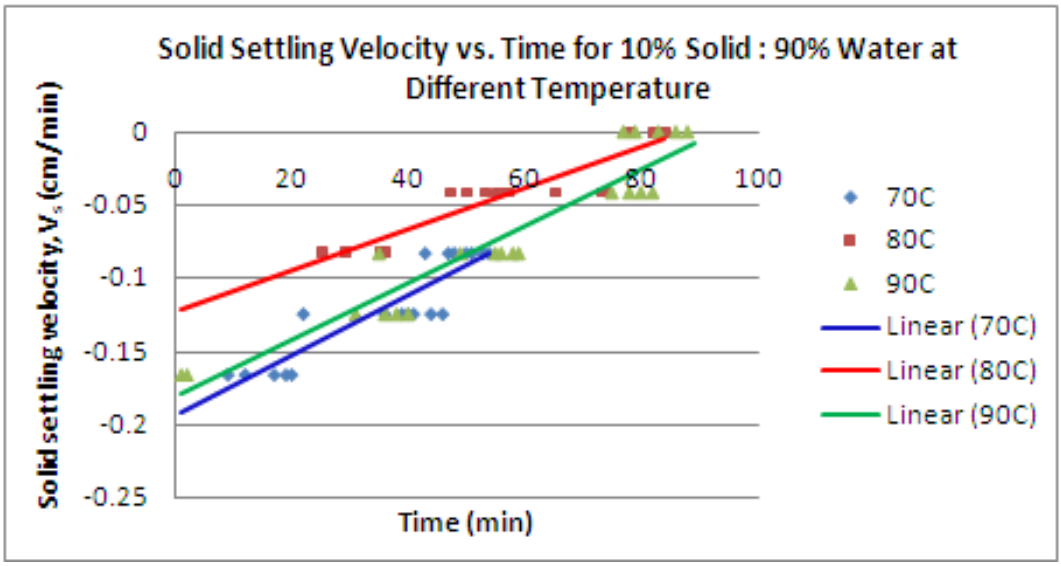


Figure 5.13 Solid settling velocities (cm/min) with time (min) in Decanter solid-water mixtures using heat treatment.

Figure 5.14 shows the rate of solid settling velocity clarifier sludge. For the clarifier sludge-water emulsion, the viscosity of the crude palm oil is lower at higher temperature. However, in Figure 5.8, it is noted that there is a sudden fall of the trend in sludge settling after a time of approximately 10 minutes. This may be caused by the presence of different contents of solid particle in the clarifier sludge (Ho and Tan 1983). As the temperature increases, the decrease of the palm oil viscosity results in a reduction of shear stress between the crude palm oil and clarifier sludge solid particles, which will then allow the solid particles to settle down more easily. As what has been observed in the experiment, the crude palm oil trapped in the clarifier sludge floated immediately to the top layer once heat was applied to it (Figure 5.15). This is due to the decrease in palm oil density as the temperature rises. Besides, small particles of solid were also found to float together with the crude palm oil and air bubbles throughout the experiment. The more heat is applied, the larger is the volume of the rising sludge. The reason for this phenomenon may be due to de-nitrification process, where nitrites and nitrates in the wastewater are converted to nitrogen gas. As nitrogen gas is formed in the sludge layer, most of it is trapped in the sludge mass. When more nitrogen gas is formed, until a certain amount, the sludge mass will become buoyant, and it will float to the

surface (Bennett 1998) The de-nitrification rate increases with increasing temperature and thus, more sludge particles floated to the surface causing the decreases in sludge settling level. In Figure 5.13, it can be observed that the best rate of solid settling velocity of sludge happens at 80ºC, which is the optimum temperature used to treat clarifier sludge water emulsion.

In addition, higher temperature will cause the polymeric moieties presents in POME to be insoluble, hence resulting in the breaking of the emulsion. All these temperature effects on breaking emulsion can be proven by Stokes law. As temperature increases, the viscosity of the emulsion decreases and thus, eases the separation rate of the mixtures.

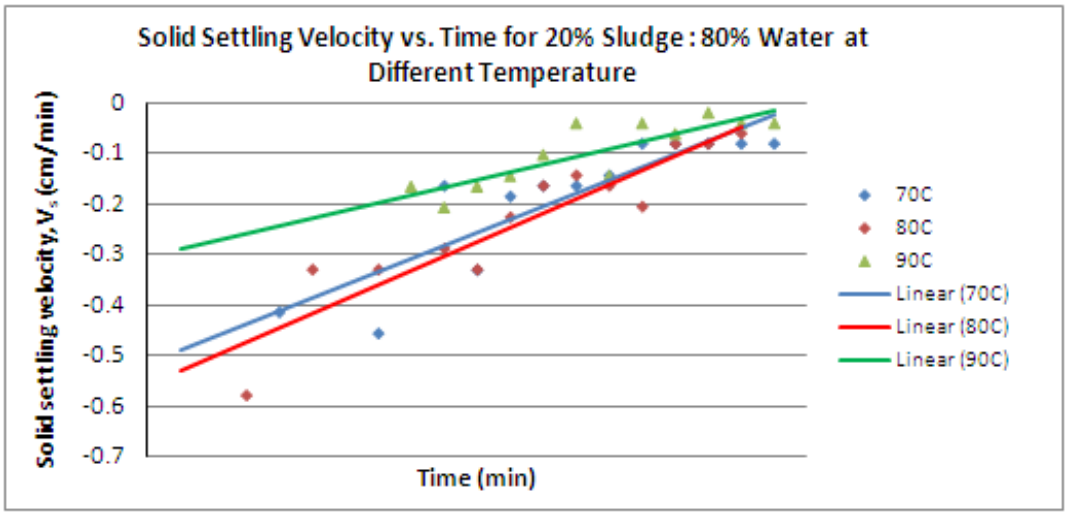


Figure 5.14 Graph of solid settling velocity versus time for the separation of 20% clarifier sludge: 80% water emulsion.

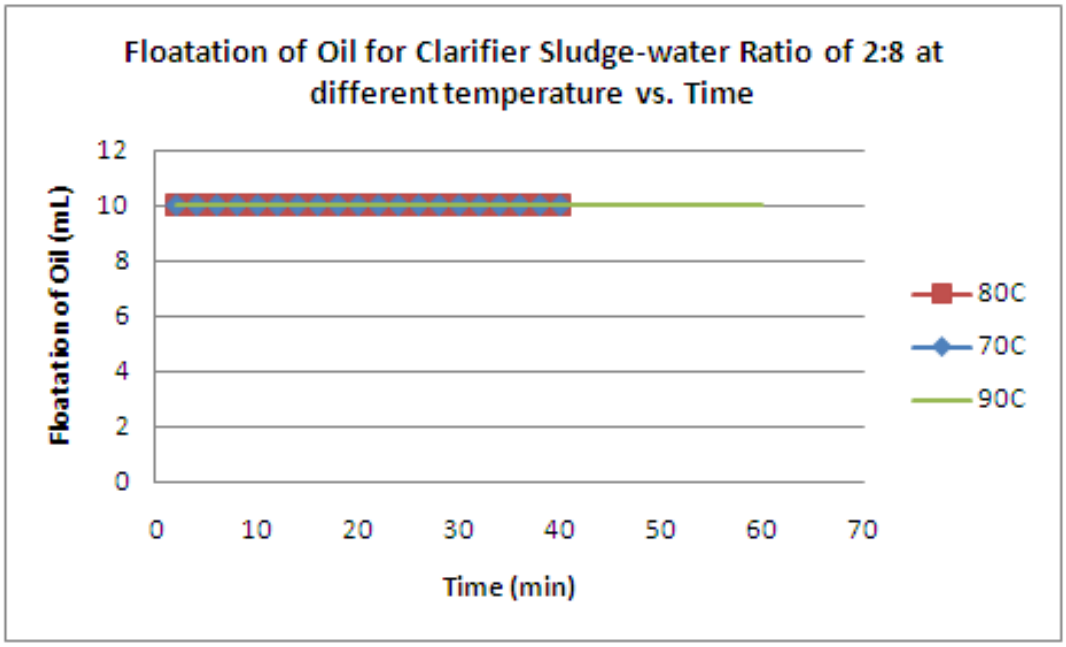


Figure 5.15 Graph of separation of clarifier sludge-water emulsion of 20% clarifier sludge and 80% water in term of oil floatation by using different temperatures.

5.6 Concluding remarks

HCl and heat treatment conditions gives very significant positive improvement in oil separation rate in palm oil-water mixture but opposite or less impact on solid settling rate in decanter solid-palm oil mixture and decanter solid-water mixture. It does give slight positive improvement in oil separation rate and solid settling rate in clarifier underflow-water mixture. However, dilution seems to be most effective in improving the solid settling rate in all three cases though this method is not permitted by the Department of Environment, Malaysia. The major discovery in this study is the effect of HCl, heat and dilution with water on the separation of oil and soild from the palm oil-solid-water emulsion that resembles POME. The contradictory responses of oil and solid particles towards the treatment of HCl make it difficult to decide whether it is feasible to use only HCl for pre-treatment of raw POME without dilution. More investigation needs to be done to compare the amount of oil and solid that remains in the suspended solid layer or supernatant layer to quantify more precisely the effect of HCl, temperature and dilution.

Chapter 6

Conclusion and Recommendation

6.1 Conclusion

A summary of the experimental results about the effects of hydrochloric acid (HCl), heat and dilution on the oil flotation and solid settling rate of different synthesized mixtures is shown in Table 6.1.

The presence of 0.5% hydrochloric acid significantly increased the flotation rate of crude palm oil/water and refined palm oil/water mixtures respectively at the range of temperature, dilution and sample size tested. The effect with refined palm oil was found to be much greater than that with crude palm oil. This observation could be attributed to the difference in the viscosity and content of the two mixtures. Another notable finding is that the effect of HCl on the floatation rate is found to be dependent on the amount of oil content in the oil-water mixtures. Increasing the concentration of HCl above 0.5% did not show any significant difference to the oil flotation rate on all tested oil-water mixtures, except for mixture with 30:70 oil-water ratios. The study shows that addition of 0.5% HCl is sufficient to significantly increase the oil flotation rate by 160 to 240 percent in the palm oil-water mixtures with 40:60 and 30:70 ratios respectively.

The effect of the HCl was also carried out on the solid settling rate of solid-water mixtures. No significant improvement on the solid settling rate in solid-water mixtures was observed and in fact, a decrease in solid settling rate was recorded in solid-palm oil mixture. However, for the palm oil-solid-water (clarifier underflow-water) mixtures, addition of dilute HCl slightly increased the solid settling rate.

As a whole, the increase rate in oil flotation rate and slight solid settlement rate by treating POME with HCl at an elevated temperature will enhance the decrease in COD which will reduce hydraulic retention time of POME treatment.

Table 6.1 a Concluding Summary of the Experimental Observation and Statistical Results

Treatment Method	Oil Flotation Rate	Solid Settlement Rate	Solid Settlement Rate	Solid Settlement Rate
	Palm oil-water mixture	Solid/Palm oil	Solid/water	Solid/Oil/Water
Addition of HCl	Increases very significantly 0.5% HCl is sufficient, no significant increase with 1.0%. Samples treated with HCl at 75^0C and samples treated without HCl at 95^0C give similar rate of oil flotation. Effect of HCl is dependent on oil-water ratio.	Slows down the rate	did not show significant effect but produce clearer supernatant.	Slight increase in rate and Also produce clearer supernatant.
Heat	Treatment with higher temperature Gives higher rate of oil flotation. The effect on oil flotation rate is not as great as that of HCl treatment.	Lesser effect in all Samples. Reverse effect caused by convection current at 90^0C. Lower temperature (80^0C) is more preferable in enhancing solid settlement.	Lesser effect in all samples Reverse effect caused by convection current at 90^0C. Lower temperature (80^0C) is More preferable in Enhancing solid settlement	Lesser effect in all samples Reverse effect caused by convection current at 90^0C. Lower temperature (80^0C) is more preferable in Enhancing solid settlement
Dilution	Dilution slows down the rate of oil flotation.	rate of solid settlement increases with increasing dilution.	rate of solid settlement increases with increasing dilution.	rate of solid settlement increases with increasing dilution most significantly in this combination.
Sample Size	Larger sample size gives faster oil Flotation rate.	No comparison done	No comparison done	No comparison done

Similarly, heat treatment of oil–water mixtures was also found to increase the oil flotation rate. However, heat treatment has little effect on solid settling rate in all samples of solid-palm oil, solid/water, and palm oil-solid-water mixtures tested. When the temperature was increased above 90^0C, a decrease in the solid settling rate was observed for the solid-oil mixtures and this is most likely the result of the convection current that was generated. This observation supports the current practice of keeping the temperature of the clarifiers in palm oil mills at a maximum temperature of 90^0C. The effect of heat treatment appeared to be independent on the concentration of oil as opposed to HCl treatment of the oil-water mixtures as shown in table 6.2 where the n value decreases from 75^0C to 95^0C.

Based on the experimental data obtained, a kinetic model on the solid settling rate was established for the solid-water and palm oil-solid-water mixtures. The result showed that the rate of change of the solid settling velocity was greatest at temperature of 80ºC. It will be a challenge for the millers to find an optimum temperature to achieve the best solid settling and oil flotation rate since the rate of oil flotation is much higher at 90ºC and above. Of notable interest is the observation that the solid-palm oil samples treated with HCl at 90ºC, although gave lower rate of solid settlement as compared to untreated samples, showed better solid settling rate as compared to samples treated with lower temperatures. It seemed that HCl had, to some extent, neutralized the effect caused by convection current.

Dilution of samples affected both the rate of oil flotation and solid settling in all cases, especially in clarifier underflow-water mixture, where no visible response in oil flotation and solid settling to HCl and heat treatment was observed when the mixture was in the raw form. Rate of oil flotation decreased as dilution increased whereas the rate of solid settlement increased with increasing dilution (Figures: 3.13, 5.2 and 5.6). The higher dilution possibly reduces the interaction between solid particles and thus speeds up the settling rate of individual particles. On the other hand, the higher dilution might reduce

the chance of collision between oil droplets and decrease the chance of coalescence and hence, a lower oil floatation rate.

6.2 Recommendation

The results obtained demonstrated the positive effect of the concurrent HCl and heat treatment on the floatation rate of the palm oil water mixture. However, more rigorous studies are required to establish the conditions for optimal separation of the oil from the solid-palm oil and water mixture or POME. Further studies need to be done on samples that closely resemble POME which is 90-95% water, 1 -3% oil and 2 – 8% solids. To this end, a pilot scale study would be essential to provide vital data for modeling the pre-treatment process of POME.

A proposed treatment system for POME as shown in Fig. 6.1 that incorporates the HCl and heat treatment, and the solid-oil separation process at the pre-treatment stage could form the alternative frame work for the future POME treatment.

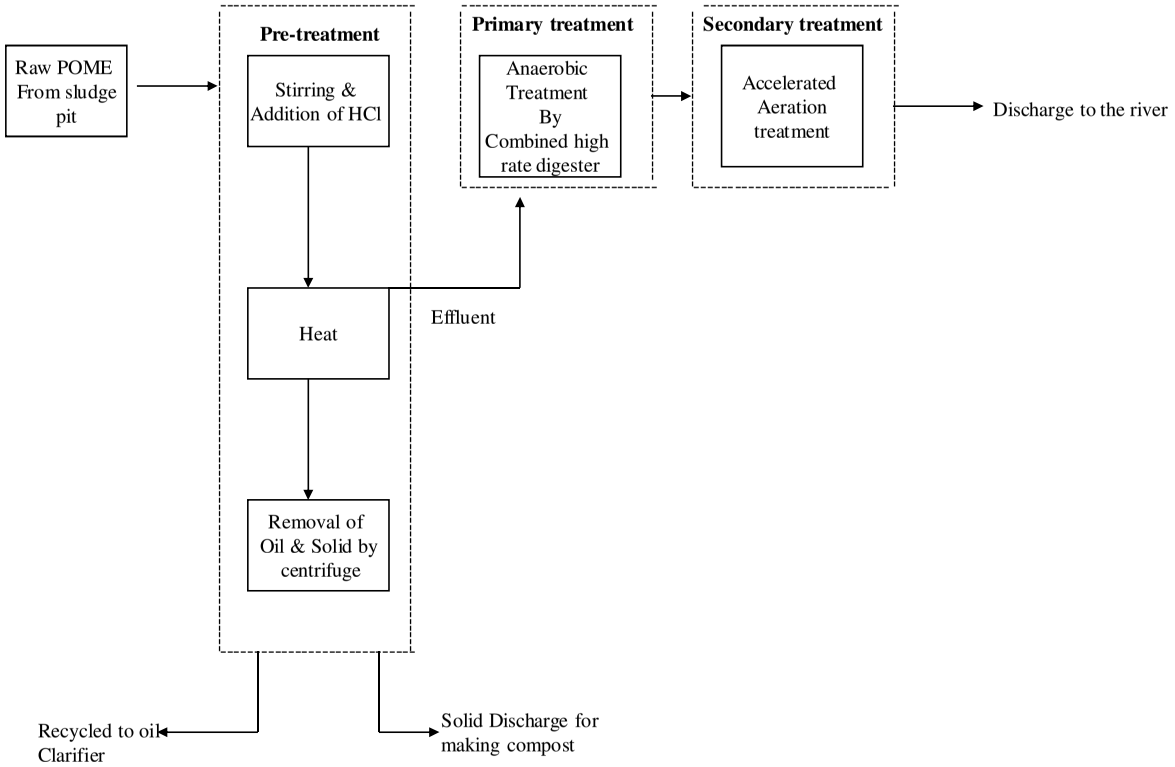


Figure 6.1: Flow chart of proposed POME treatment system

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Appendix A

Data Analysis for Rate of Oil Flotation

Kinetic model was used for the analysis of all the data obtained from different experiments done on the effect of different treatments on both Crude palm oil-water and Refine palm oil-water mixtures. The development of kinetic models would enable future validation of the results obtained at present to ensure a safer application in POME treatment.

To date there is no single universally accepted kinetic rate law of oil floatation (Bennett, 1998). The kinetic order of oil floatation depends on the concentration of oil inside the oil-water emulsion. For oil concentration between 100 – 500 ppm, it was reported in (Pal R., Masliyah J., 1990) that the oil floatation follows first order kinetic. For a very high oil concentration (above 25% by wt), the overall kinetic order is 0.6. These wide differences imply that the oil particle floatation differs from solid particle floatation (Gu, Chiang, 1999).

We adopted in our case a macro kinetic approach modeling to the oil floatation by assuming that it's kinetic follows the generalized form:

$$R_f = kC_0^n \qquad \text{(A.1)}$$

Where R_f is the rate of oil flotation and C_o is the oil concentration inside the oil-water emulsion. (Wong F. et. al 2005)

Applying the mass balance on oil in the oil-water emulsion layer, we can obtain the following equation:

$$\frac{d(V_e C_0)}{dt} = -R_f V_e \qquad \text{(A.2)}$$

But the mass of oil remaining inside the oil-water emulsion (V_eC_o) is also given by:

$$V_e C_0 = \rho_0 (V_i - V_0) \qquad \text{(A.3)}$$

Where V_i, V_e, V_o are the volumes of total oil, oil-water emulsion and oil layer, respectively and ρ_o is the oil density.

From (A.2) and (A.3), we get:

$$\rho_0 \frac{dV_0}{dt} = R_f V_e \tag{A.4}$$

We can relate the V_e to the total volume of oil-water emulsion initially (total cylinder volume) V_c and V_o.

$$V_e = V_c - V_0 \tag{A.5}$$

Furthermore C_o can be expressed as:

$$C_0 = \frac{\rho_0 (V_i - V_0)}{V_c - V_0} \tag{A.6}$$

Substituting (A.5) into (A.4) and then gathering the similar terms together yield:

$$\frac{\rho_0}{V_c - V_0} \frac{dV_0}{dt} = R_f \tag{A.7}$$

Furthermore, (A.7) can be expressed as:

$$-\rho_0 \frac{d \ln(V_c - V_0)}{dt} = R_f \tag{A.8}$$

In order to obtain the values for k and n in (A.1) form the experiment data, we arrange (A.8) in a log form as:

$$R_f = \ln k + n \ln C_0 \tag{A.9}$$

Where, R_f and C_o can be calculated from (A.4) and (A.6). From the plot of (A.9) the values of k and n can be calculated. For example, Figure A-1 shows a typical plot of *ln* (R_f) versus *ln* (C_o) obtained from experiment data.

Modeling of Oil-Separation Rate

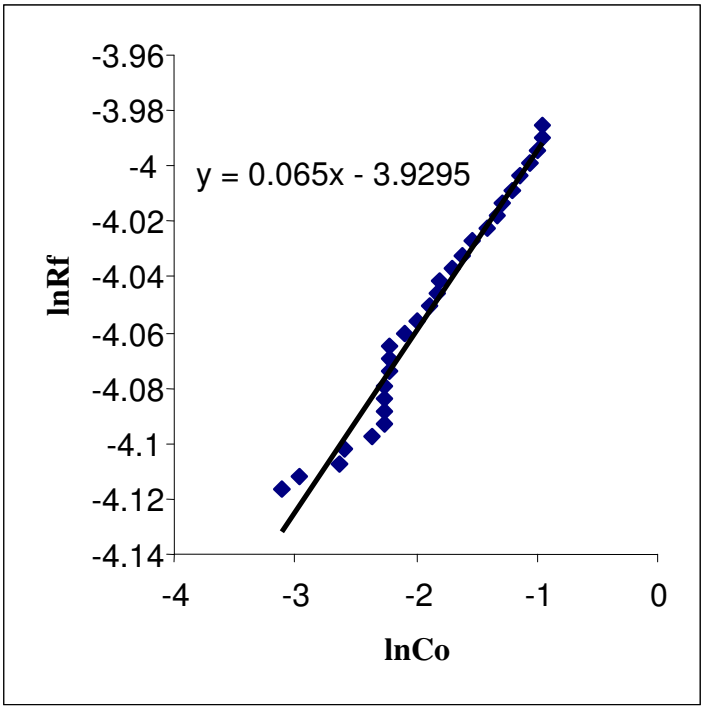

Figure A-1 Log-log plot of floatation rate R_F versus oil concentration C_o in the oil-water emulsion layer (Wong et al, 2005).

Appendix B

Hydrochloric Acid (HCl)

With the understanding from the literature review in chapter 2, acid cracking is one of the chosen methods for the study of oil and solid separation from POME in this research and a commercial grade Hydrochloric acid (HCl) was used as the reagent for the following reasons:

It is one of the least hazardous strong acids to handle that produces less reactive and non-toxic chloride ion. It is quite stable, maintaining their concentrations over time. These attributes therefore serves as the motivation in using HCl to be the chemical as emulsion breaker in this research, instead of H_2SO_4, which is comparatively cheaper. The concentration of HCl to be added to oil-water mixture was as follows:
0.5 And 1.0 (v/v %).

Equipment and Apparatus

- Hot plates (Figure 3.1) – to provide heat to the water bath used for heating of sludge-palm oil mixtures.
- 100 ml graduated measuring cylinders were used as containers for the study of the rate of solid settlement in chapter 4.
- 5 liters beakers – used as water-bath for heating of sludge-palm oil mixtures.
- 

  Figure B-1 A Panasonic MX-801S blender for mixing of sludge-palm oil, palm oil-water and all other synthetic POME mixtures before testing.
- 0 – 100^{0}C thermometers for measurement of temperatures.